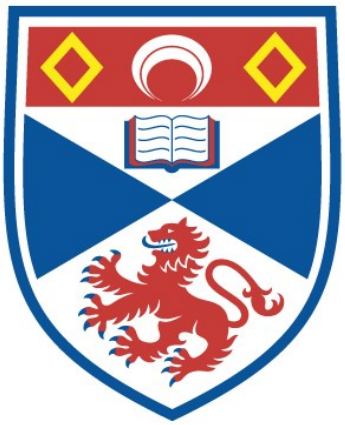
THE EFFECT OF LOCAL FIELD CORRECTIONS ON THE TRANSPORT PROPERTIES OF SOLIDS

Mesude Saglam

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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A thesis presented by

Mesude Sağlam

to the

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Declaration

The accompanying thesis is my own composition. It is based on work carried out by me and no part of it has previously been presented in application for a Higher Degree.

I was admitted as a research student under Ordinance General No. 12 in October 1973, and as a candidate for the degree under this ordinance in October 1974.

Certificate

I certify that the conditions of the Ordinance and Regulations have been fulfilled.

Research Supervisor

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CONTENTS

INTRODUCTION

The purpose of this work is to investigate local field type corrections to electrical transport properties and in particular small polaron hopping conductivity. The question of local field corrections to transport properties has been considered for some time[23]. Recently this question has become of particular interest for small polaron hopping conduction[1]. Such corrections were considered as a possible explanation for the large jump parameters inferred in fitting the electric field dependence of the electrical conductivity of certain transition metal oxide glasses in which conduction is believed to occur via thermally activated small polaron hopping[2,3].

Local field corrections are well established in determining the dielectric constant and optical properties at a single atomic site. Tessman et al[4] have shown that the assumption of a normal Lorentz term gives excellent agreement between computed and measured polarizabilities in alkali halide crystals at optical frequencies. Adler[5] has proved, using a self-consistent field theory, that the standard Lorentz term arises in the tight binding limit. Also a full quantum mechanical treatment of the frequency and wave-number dependent dielectric constant including local field effect has been given by Wiser[6]. It is shown that the dielectric constant splits into an atomic term that describes the motion of the electron around each atom and an acceleration term which describes the motion from atom to atom, and that acceleration term contains no local field correction.

Lidiard[7] has discussed Lorentz type corrections to the diffusion coefficient in ionic conductivity. He argued that no Lorentz correction should be applied, since the Lorentz cavity must always be centred on the hopping carrier; thus, the Lorentz internal

field can do no work as the carrier moves from one site to another. This view is strongly supported by the close agreement between ionic diffusion coefficients obtained from conductivity data and NMR relaxation and isotopic diffusion[8].

It has been argued by Munn in several papers[9,10] without detailed justification that the microscopic mobility does give the polaron velocity in terms of a local field. This argument is in conflict with that of Lidiard[7]. However this question had not been considered explicitly for the case of electrical transport in the hopping limit.

It is the intent of the present work to study the local field problem. In the first chapter we give a general description of the local electric field concept which is straight review. Chapters II and III are concerned with the question of local field corrections to the small polaron hopping conduction and the Hall mobility. In chapter IV the results of chapter II are applied to ac impurity hopping conduction. Finally, in chapter V we study the band motion of electrons using a theory of transport based on quantum mechanical principles.

To consider the local field corrections to any kind of hopping mechanism, it is essential to determine the elementary site to site jump rate for a polarizable dielectric which characterizes a hop from one site to another. Attention being restricted to small polaron hopping, we show that in the classical high temperature site jump regime the jump rate between nearest neighbour sites $\underset{\sim}{q}$ and $\underset{\sim}{q}''$ is given by

$$\omega_T(\underset{\sim}{q} \to \underset{\sim}{q}'') = \omega_T^{\circ}(\underset{\sim}{q} \to \underset{\sim}{q}'') \exp\left[\frac{e\underset{\sim}{E}_0 \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') + (W_{\underset{\sim}{q}}^{f} - W_{\underset{\sim}{q}''}^{f})}{2kT}\right],$$

where $\omega_T^{\circ}(\underset{\sim}{q} \to \underset{\sim}{q}'')$ denotes the jump rate in the absence of the external field and induced polarization and $W_{\underset{\sim}{q}}^{f}$ is the dipolar

energy at site $\underset{\sim}{q}$. Therefore the question of local field correction to small polaron hopping conduction reduces to an evaluation of $[W_q^p - W_{q'}^p]$ for nearest neighbour sites $\underset{\sim}{q}$ and $\underset{\sim}{q}''$. It then follows that if the sites $\underset{\sim}{q}$ and $\underset{\sim}{q}''$ are crystallographically equivalent, the evaluation of $[W_q^p - W_{q''}^p]$ becomes very simple. This is due to the fact that for every dipole at $\underset{\sim}{q}'$ which contributes to W_q^p , there is a corresponding dipole at $\underset{\sim}{q}' + (\underset{\sim}{q}'' - \underset{\sim}{q})$ which contributes identically to $W_{q''}^p$. So in taking the difference short range and Lorentz contributions cancel. This cancellation occurs in detail until the outer surfaces of the specimen are reached. Taking the specimen to be in the shape of a general ellipsoid of revolution, $[W_q^p - W_{q''}^p]$ becomes

$$W_q^p - W_{q''}^p = e\,\underset{\sim}{E}_1 \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') ,$$

where $\underset{\sim}{E}_1$ is the depolarization field. This contribution, when added to that of external charges, gives just the macroscopic field, $\underset{\sim}{E}_{mac}$, unmodified by the local field corrections.

However if $\underset{\sim}{q}$ and $\underset{\sim}{q}''$ are inequivalent sites, the short range contributions to the dipolar potentials at the two sites do not cancel although Lorentz contributions do. This leads to local field type corrections to the jump rate, and hence to the hopping conductivity as well. The resulting corrections are found to be negligible at low fields $e\underset{\sim}{E}_{mac}(\underset{\sim}{q} - \underset{\sim}{q}'') < kT$ but considerable at higher fields. Therefore local field corrections to hopping transport between crystallographically inequivalent sites are associated with the high field behaviour of the system.

Recently Munn[11] reanalysed local field effects using classical electrostatics. He used an expression for the macroscopic field due to a set of polarizable point sublattices to calculate the work done in moving a charge between two sites in an applied electric field. He then applied the result to hopping mobilities ignoring polaron effects on the lattice around the carrier. His conclusions agree with those of

1.1 General description of the present work:

Chapter I : The general theory of the local electric field and the macroscopic electric field.

In this opening chapter we give a review of the necessary concepts needed in the study of local field corrections in the subsequent chapters.

Chapter II : The question of local field corrections to the small polaron hopping conduction.

This chapter constitutes the main part of this thesis. In the first part, section (2.1), we give a survey of experimental results which suggest the possibility of the local field corrections to the small polaron hopping conductivity.

In section (2.2), we review the small polaron theory in the one-dimensional molecular-crystal model of Holstein[16,17].

In section (2.3), we study the small polaron motion for a polarizable dielectric within the framework of the one-dimensional molecular-crystal model. To consider local field corrections, first, we extend the molecular-crystal model to three dimensions. Secondly, the effect of a constant applied field $\underset{\sim}{E}_o$ and induced dipole moments are incorporated into the Hamiltonian of the system. A discussion of the physical assumptions and a detailed derivation of the fundamental equation of motion are presented in section (2.3a).

In section (2.3b), the elementary jump rates are calculated in a classical-occurrence probability treatment, previously introduced by Holstein, which applies at temperatures large compared to the Debye temperature. The basic feature of this approach is that the dominant contributions to the small polaron mobility occur at a momentary coincidence of the two site energies. In this case the jump rate between nearest neighbour sites $\underset{\sim}{g}$ and $\underset{\sim}{g}''$ is given by

$$\omega_T(\underset{\sim}{q} \to \underset{\sim}{q}') = \omega_T^0(\underset{\sim}{q} \to \underset{\sim}{q}') \exp\left[\frac{e\underset{\sim}{E}_0 \cdot (\underset{\sim}{q} - \underset{\sim}{q}') + (W_{\underset{\sim}{q}}^p - W_{\underset{\sim}{q}'}^p)}{2kT}\right]$$

from which it is seen that local field corrections may arise from the difference in dipolar energies, $[W_{\underset{\sim}{q}}^p - W_{\underset{\sim}{q}'}^p]$, for nearest neighbour sites $\underset{\sim}{q}$ and $\underset{\sim}{q}'$.

In section (2.4), the evaluation of $[W_{\underset{\sim}{q}}^p - W_{\underset{\sim}{q}'}^p]$ is carried out in detail for a sample in the shape of a general ellipsoid of revolution. The work presented in this section has already been published as a short letter[22].

An extension of the present results to the case of hopping between inequivalent sites is presented in section (2.5). It is shown that the local field type corrections can be neglected for low fields but can be large for high fields.

In section (2.6), the application of the present results to the glasses, where long-range order disappears, is demonstrated.

Chapter III: The question of the local field correction to the Hall mobility of the small polaron.

In this chapter we investigate the local field correction to the Hall mobility of the small polaron on the basis of the theory developed by Friedman and Holstein[19]. As discussed in their paper, the Hall mobility is understood to arise from interference between direct hops from one site $\underset{\sim}{q}_1$ to a neighbour site $\underset{\sim}{q}_2$ and indirect hops between the same site via a third intermediate site $\underset{\sim}{q}_3$.

In section (3.1), we briefly review the theory of Hall mobility of reference (19).

In section (3.2) we extend the theory of the Hall mobility of the small polaron to a polarizable dielectric. Similar generalizations, as in chapter II, are introduced here as well.

A discussion of the physical assumptions and a detailed derivation of the fundamental equation of motion are presented in section (3.2a).

In section (3.2b), magnetic and electric field modified jump rates for a polarizable dielectric are calculated for the elementary three-site configuration. It turns out that the local field problem reduces to evaluation of $\left(W^{p}_{\underset{\sim}{q}_1} - W^{p}_{\underset{\sim}{q}_2} \right)$ and $\left(W^{p}_{\underset{\sim}{q}_1} - W^{p}_{\underset{\sim}{q}_3} \right)$ for three mutually neighbour sites at $\underset{\sim}{q}_1$, $\underset{\sim}{q}_2$ and $\underset{\sim}{q}_3$. Therefore the results of chapter II equally apply to the Hall mobility of the small polaron as well.

In section (3.3), the application of the present theory to the glasses is given. A modification of the transfer integral J, applicable to the d-levels of the transition metal ions, is calculated.

Chapter IV : Local field corrections to ac impurity hopping conductivity.

In this chapter we apply the present results to ac impurity hopping conduction. It is noted that the results found for small polaron hopping can be generalized to any kind of thermally activated hopping mechanism. The reason for this is that for each case the jump rate will depend on the difference in energy at two sites that hopping occurs.

The particular theory of ac impurity hopping conduction which we use is the pair approximation of Pollak and Geballe[33].

In section (4.1), we give a review of experiments on ac impurity hopping conductivity.

Section (4.2) summarizes the pair approximation.

In section (4.3), we study the modification of the pair approximation for a polarizable dielectric. Again, it turns out that the results of chapter II equally apply to the ac impurity hopping conductivity as well.

Chapter V : Quantum theory of electric transport in the presence of induced dipoles.

In this chapter we generalize the results of hopping motion to band motion of electrons using a theory of transport based on quantum mechanical principles. We develop such a theory with the density matrix formalism of Kohn and Luttinger[12].

We carry out the calculations for the transport in one energy band. It turns out that, in the presence of induced dipoles, the net electric field appearing in the transport equation is again just the macroscopic field, $\underline{E}_{mac}$. However, if interband transitions were considered we would expect local field type corrections in line with the result for hopping between different sublattices.

CHAPTER I

THE GENERAL THEORY OF THE LOCAL ELECTRIC FIELD AND THE MACROSCOPIC ELECTRIC FIELD

Local electric field: The local electric field, $\underset{\sim}{E}_{loc}$, acting on an ion in a solid is the sum of the external field, $\underset{\sim}{E}_{o}$, and the field due to all other induced dipoles in the medium. For a cubic lattice of equal and parallel dipoles, the specimen can be treated as uniform dielectric as long as it has the shape of a general ellipsoid of revolution[24]. The standard method of summing the dipole fields of the other induced dipoles is first to sum individually over a moderate number of neighbouring dipoles inside an imaginary Lorentz sphere concentric with the reference ion, defining the field $\underset{\sim}{E}_{3}$, which vanishes at a reference site with cubic symmetry, then to sum the dipole fields outside the sphere. Since the medium is uniformly polarized, the second contribution will be $\underset{\sim}{E}_{1} + \underset{\sim}{E}_{2}$, where $\underset{\sim}{E}_{1}$ is the depolarization field associated with the dipoles on the outer boundary and $\underset{\sim}{E}_{2}$ is the Lorentz field associated with the surface of the spherical cavity, Figure (1.1). Thus, $\underset{\sim}{E}_{loc}$ can be expressed as the following sum of terms :

$$\underset{\sim}{E}_{loc} = \underset{\sim}{E}_{o} + \underset{\sim}{E}_{1} + \underset{\sim}{E}_{2} + \underset{\sim}{E}_{3} \quad . \tag{1.1}$$

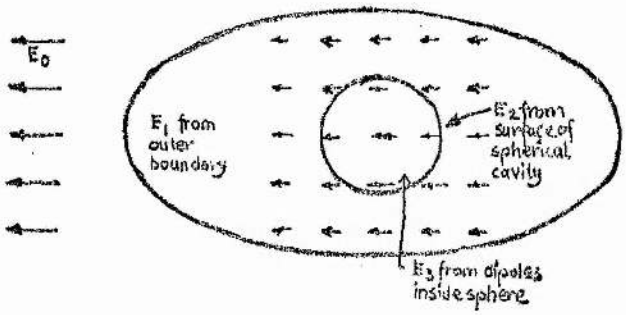

Figure (1.1)

Consider the electrostatic potential due to a dipole $\underset{\sim}{P_i}$ located at the source point $\underset{\sim}{r_i}$, at the point $\underset{\sim}{r}$,

$$\phi_i(\underset{\sim}{r}) = \frac{\underset{\sim}{P_i}\cdot(\underset{\sim}{r}-\underset{\sim}{r_i})}{|\underset{\sim}{r}-\underset{\sim}{r_i}|^3} = \underset{\sim}{P_i}\cdot\underset{\sim}{\nabla}_{(r-r_i)}\frac{1}{|\underset{\sim}{r}-\underset{\sim}{r_i}|} = \underset{\sim}{P_i}\cdot\underset{\sim}{\nabla}_{r_i}\frac{1}{|\underset{\sim}{r}-\underset{\sim}{r_i}|} \quad (1.2)$$

The total electrostatic potential due to all dipoles contained in the volume outside of the Lorentz sphere is

$$\phi(\underset{\sim}{r}) = \sum_i \underset{\sim}{P_i}\cdot\underset{\sim}{\nabla}_{r_i}\frac{1}{|\underset{\sim}{r}-\underset{\sim}{r_i}|} = \int \underset{\sim}{P}\cdot\underset{\sim}{\nabla}_{r_1}\frac{1}{|\underset{\sim}{r}-\underset{\sim}{r_1}|}\,dV_1$$

$$= \int dV_1\left[-\frac{1}{|\underset{\sim}{r}-\underset{\sim}{r_1}|}\,\underset{\sim}{\nabla}\cdot\underset{\sim}{P} + \underset{\sim}{\nabla}\cdot\frac{\underset{\sim}{P}}{|\underset{\sim}{r}-\underset{\sim}{r_1}|}\right], \quad (1.3)$$

where $\underset{\sim}{P}$ is the macroscopic polarization i.e. dipole moment per unit volume averaged over the volume of the crystal cell. Here, dV_1 is the volume element of the space outside the Lorentz sphere. In practice if the radius of the Lorentz sphere is large, the replacement of the above summation by a continuous integration is justified.

Since $\underset{\sim}{P}$ is uniform; then $\nabla \cdot \underset{\sim}{P} = 0$. And by the divergence theorem Eq. (1.3) becomes

$$\phi(r) = \int_{\text{[over the outer surface]}} dS \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{r} = \int_{\text{[over the outer surface]}} dS \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{r} + \int_{\text{[over the Lorentz sphere]}} dS \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{r} = \phi_1 + \phi_2 \qquad (1.4)$$

where

$$\phi_1 = \int_{\text{[over the outer surface]}} dS \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{r} \quad , \qquad (1.5)$$

$$\phi_2 = \int_{\text{[over the Lorentz sphere]}} dS \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{r} \quad . \qquad (1.6)$$

We define $\underset{\sim}{E}_1$ and $\underset{\sim}{E}_2$ such that

$$\underset{\sim}{E}_1 = -\underset{\sim}{\nabla}\phi_1 = -\underset{\sim}{\nabla}\left[\int_{\text{[over the outer surface]}} dS \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{r}\right] \quad , \qquad (1.7)$$

$$\underset{\sim}{E}_2 = -\underset{\sim}{\nabla}\phi_2 = -\underset{\sim}{\nabla}\left[\int_{\text{[over the Lorentz sphere]}} dS \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{r}\right] \quad . \qquad (1.8)$$

Depolarization field, $\underset{\sim}{E}_1$: From Eq. (1.7) it is seen that the depolarization field $\underset{\sim}{E}_1$ is defined as the field of the surface charge density $\underset{\sim}{P}\cdot\underset{\sim}{n}$ on the outer surface of a simply-connected body. The depolarization field tends to oppose the applied field $\underset{\sim}{E}_0$ as in figure (1.2). Specimens in the shape of a general ellipsoid of revolution (a class that includes spheres, cylinders and discs as limiting form) have an advantageous property: A uniform polarization produces a uniform depolarization field. If P_x , P_y , P_z are the components of the polarization $\underset{\sim}{P}$

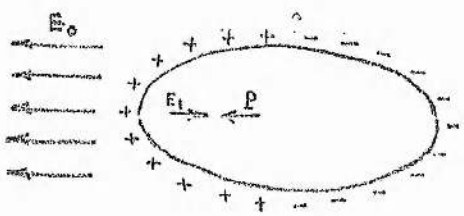

Figure (1.2)

referred to the principle axes of an ellipsoid, then the components of the depolarization field are written as

$$E_{1x} = -N_x P_x \; ; \; E_{1y} = -N_y P_y \; ; \; E_{1z} = -N_z P_z \; . \qquad (1.9)$$

Here N_x, N_y, N_z are the depolarization factors, their values depend on the ratio of the principle axes of the ellipsoid. The N's are positive and satisfy the sum rule:

$$N_x + N_y + N_z = 4\pi \quad (\text{in CGS units}) \; . \qquad (1.10)$$

Lorentz field, $\underset{\sim}{E}_2$: From Eq. (1.8) it is seen that the Lorentz field $\underset{\sim}{E}_2$ is defined as the field of surface charge density $\underset{\sim}{P} \cdot \underset{\sim}{n}$ on the internal surface of the Lorentz cavity. It was first calculated by Lorentz. If θ is the polar angle referred to the polarization direction as axis (figure 1.3) the surface charge density on the surface of the cavity is $P \cos\theta$. The electric field at the centre of the spherical cavity of radius R is

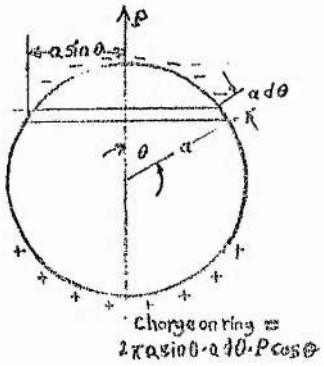

Figure (1.3)

$$\underset{\sim}{E}_2 = \int_0^{\pi} (R^{-2})(2\pi R \sin\theta)(R\, d\theta)(P \cos\theta)\cos\theta \, d\theta$$

$$= \frac{4\pi}{3} \underset{\sim}{P} \qquad (1.11)$$

The field, $\underset{\sim}{E}_3$: The field, $\underset{\sim}{E}_3$, which is defined as the field due to dipoles inside the cavity, is the only term that depends on the crystal structure. For cubic symmetry, $\underset{\sim}{E}_3$ is zero.

$$E_3 = 0 \; , \text{ For cubic symmetry} \; . \qquad (1.12)$$

So the total local field at a cubic site is

$$\underset{\sim}{E}_{loc} = \underset{\sim}{E}_0 + \underset{\sim}{E}_1 + \frac{4\pi}{3}\underset{\sim}{P} \quad . \tag{1.13}$$

Macroscopic field, $\underset{\sim}{E}_{mac}$: The macroscopic field, $\underset{\sim}{E}_{mac}$ is defined as the space average electric field over the volume of a unit cell of the crystal. It will be shown that for a sample in the shape of a general ellipsoid of revolution, $\underset{\sim}{E}_{mac}$ is equal to $\underset{\sim}{E}_0 + \underset{\sim}{E}_1$: This result can be seen by considering a long thin specimen in an external field $\underset{\sim}{E}_0$ parallel to the long axis. For this geometry, the field component parallel to the axis but just outside the specimen must be $\underset{\sim}{E}_0$. Now the average field component parallel to the axis but over any path just inside the specimen must also be $\underset{\sim}{E}_0$. This is because the integral of the electric field around a closed path is zero $\left(\underset{\sim}{\nabla} \times \underset{\sim}{E}_{mac} = 0\right)$. So we have

$$\underset{\sim}{E}_{mac} = \underset{\sim}{E}_0 \quad , \quad \text{for a long thin specimen .} \tag{1.14}$$

Meanwhile we note that for the microscopic field $\underset{\sim}{E}_{mic}(r)$ at any point in the medium we can write an expression similar to Eq. (1.1),

$$\underset{\sim}{E}_{mic}(r) = \underset{\sim}{E}_0 + \underset{\sim}{E}_1(r) + \underset{\sim}{E}_2(r) + \underset{\sim}{E}_3(r) \, . \tag{1.15}$$

But in this case $\underset{\sim}{E}_3(r)$ will not necessarily be zero for a cubic crystal. If we apply the above discussion to Eq. (1.15), we can write the macroscopic field for a long thin specimen again:

$$\underset{\sim}{E}_{mac} = \langle \underset{\sim}{E}_{mic}(r) \rangle = \langle \underset{\sim}{E}_0 \rangle + \langle \underset{\sim}{E}_1(r) \rangle + \langle \underset{\sim}{E}_2(r) \rangle + \langle \underset{\sim}{E}_3(r) \rangle \, , \tag{1.16}$$

where $\langle\ \rangle$ means average over a unit cell. Noting that $\langle \underset{\sim}{E}_0 \rangle = \underset{\sim}{E}_0$ and $\langle \underset{\sim}{E}_1 \rangle = 0$ and comparing (1.14) with (1.16) we see that

$$\langle \underset{\sim}{E}_2(r) \rangle + \langle \underset{\sim}{E}_3(r) \rangle = 0 \quad . \tag{1.17}$$

Now the result (1.17) can be generalized to any specimen of any shape, because neither E_2 nor E_3 is shape dependent. So for a specimen in the shape of a general ellipsoid of revolution (where we have a uniform depolarization field E_1) the macroscopic field becomes

$$\underset{\sim}{E}_{mac} = \langle \underset{\sim}{E}_{mic}(r) \rangle = \underset{\sim}{E}_0 + \underset{\sim}{E}_1 \ , \tag{1.18}$$

because $\langle \underset{\sim}{E}_0 \rangle = \underset{\sim}{E}_0$ and $\langle \underset{\sim}{E}_1 \rangle = \underset{\sim}{E}_1$.

Using the definition of the macroscopic field given by Eq. (1.18), Eq. (1.13) becomes

$$\underset{\sim}{E}_{loc} = \underset{\sim}{E}_{mac} + \frac{4\pi}{3} \underset{\sim}{P} \ . \tag{1.19}$$

Thus the field acting on an ion at a cubic site is the macroscopic field, the field appearing in Maxwell's equations plus the Lorentz field $\frac{4\pi}{3} \underset{\sim}{P}$. From Eq. (1.19) it is clearly seen that the local field is always larger than the macroscopic field :

$$|\underset{\sim}{E}_{loc}| > |\underset{\sim}{E}_{mac}| \ . \tag{1.20}$$

CHAPTER 2

THE QUESTION OF THE LOCAL FIELD CORRECTIONS TO THE SMALL POLARON HOPPING CONDUCTION

2.1 Experimental evidences:

Transition metal oxide glasses, especially those based on V, Fe, Cu and Mo ions and pure and doped tungstates have been extensively investigated by Austin et al[1]. It has been shown that ohmic behaviour occurs for fields up to 10^5 V cm^{-1}. At higher fields the conductivity varies as

$$\sigma(E_o) = \sigma(0)\,\frac{\sinh[eaE_o/2kT]}{eaE_o/2kT},$$

where e is the magnitude of the charge of the electron, a is the jump parameter and E_o is the applied electric field. This expression corresponds to a simple field dependent small polaron hopping mobility[13-15]. It is generally agreed that[2,3] in these materials, because of the mixed valency, conduction takes place by small polaron hopping between transition metal ion sites for example: ($V^{4+} \rightarrow V^{5+}$) in vanadates and ($Fe^{2+} \rightarrow Fe^{3+}$) in ferrites. The observed temperature dependence of the conductivity can be explained on the basis of the small polaron hopping mechanism.

The glass melts of the above compositions were prepared by mixing appropriate transition metal oxides and P_2O_5 as in table (2.1). But the experimental jump parameters inferred in fitting the electric field dependence of the electrical conductivity are always found to be 4-6 times larger than the average transition metal ion spacing. This seems unreasonable, because, the local wave functions, being 3d waves, should give negligible overlap J for sites separated by

such a large distance. Table (2.1) also shows an enhancement factor (P) , calculated from the ratio of the effective hopping distance and the mean transition metal ion spacing.

Composition mol% MO	P_2O_5	TMI spacing A°	W_H eV	Jump parameter A°	Enhancement factor: P
V_2O_5 80	20	3.99	0.35	18	> 4.5
V_2O_5 70	30	4.17	0.38	17	4.1
V_2O_5 60	40	4.37	0.40	24	5.5
Fe_2O_3 38	62	4.70	0.59	31	> 6.6
Cu O 54	46	4.80	1.00	28	5.8
WO_3 66.7	33.3	4.55	0.39	43	9.5

Table (2.1) Compositions and electrical characteristics of glasses.

These authors discuss several models to increase the effective jump parameter in the $\sinh$ formula, but in each case they find the increase too small to account for the enhancement factor. An alternative way of viewing the data is to allow for a larger electric field in the $\sinh$ formula. As a possible explanation, it has been thought that the electric field might be a Lorentz type local field which is larger than the applied field:

$$\underset{\sim}{E}_{loc} = \underset{\sim}{E} + \frac{4\pi}{3}\underset{\sim}{P} ,$$

where P is the induced polarization in the medium. A large local field would lead to smaller values of the jump distance, a .

Figure (2.1) shows the conductivity versus electric field for certain vanadium phosphate glasses. As it is seen ohmic behaviour

occurs up to fields $10^5 V\,cm^{-1}$ and a subsequent rapid development of non-ohmic behaviour from the sinh function.

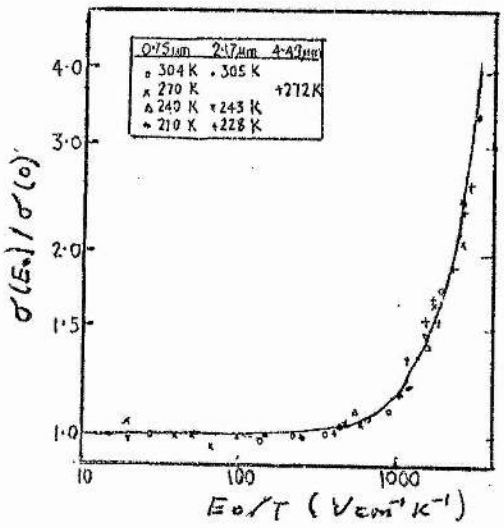

Figure (2.1) $\sigma(E_0)/\sigma(0)$ against E_0/T for a glass of composition 70 mol% V_2O_5 : 30 mol% P_2O_5. Thicknesses and temperatures shown on the diagram. The full line represents $(\sinh mx)/mx$.

REVIEW OF THE SMALL POLARON MOTION

2.2a Introduction:

The particular theory of the small polaron on which the present study is based, is the one-dimensional molecular-crystal-model of Holstein[16,17]. In this model, in the absence of the excess carrier, the system is taken to be a linear chain consisting of diatomic molecular sites with fixed centres of gravity and orientations, but with variable inter-nuclear separations, X_n, which play the role of lattice vibrational coordinates. The state of the small polaron is the state in which an excess electron (or hole) is on a definite ion while that diatomic molecule vibrates about the displaced position which depends on the location of the electron. The motion of the excess charge in this model is formulated in terms of the tight-binding approximation in which the total wave function, Ψ, is represented as a linear superposition of "molecular" electron wave functions $\phi(\underset{\sim}{r}-n\underset{\sim}{a}, X_n)$:

$$\Psi(\underset{\sim}{r}, X_1, \ldots, X_N) = \sum_n a_n(X_1 \ldots X_N)\ \phi(\underset{\sim}{r}-n\underset{\sim}{a}, X_n)\ , \qquad (2.1)$$

here $\underset{\sim}{r}$ is the coordinate of the electron, and X_n is the inter-nuclear displacement (from equilibrium) of the n^{th} site. The local molecular wave functions $\phi(\underset{\sim}{r}-n\underset{\sim}{a}, X_n)$ centred at site n depend parametrically on the internuclear coordinates, X_n, as indicated. The equation satisfied by a particular $\phi(\underset{\sim}{r}-n\underset{\sim}{a}, X_n)$ is

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\underset{\sim}{r}-n\underset{\sim}{a}, X_n)\right]\phi(\underset{\sim}{r}-n\underset{\sim}{a}, X_n) = E(X_n)\,\phi(\underset{\sim}{r}-n\underset{\sim}{a}, X_n)\,, \qquad (2.2)$$

where $U(\underset{\sim}{r}-n\underset{\sim}{a}, X_n)$ is the contribution of the n^{th} molecule to the effective one-electron potential and is assumed to be short-range, and where $E(X_n)$ is the eigenvalue of (2.2).

The site occupation amplitudes a_n are functions of all the displacements and satisfy the following fundamental equations of motion:

$$i\hbar \frac{\partial a_n}{\partial t} = \left[-A X_n + \sum_m \left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X_m^2} + \frac{M\omega_0^2}{2} X_m^2 + \frac{M\omega^2}{2} X_m X_{m+1} \right) \right] - J(a_{n+1} + a_{n-1}) \quad . \tag{2.3}$$

The term $(-A X_n)$ represents a phenomenological electron-lattice interaction as a linear function of the vibrational coordinates of the occupied site. The interaction is thus assumed to have an entirely local character.

The sum over m includes the vibratory kinetic and potential energies of the molecules. They are expressed in terms of M, the reduced mass of the molecules, and ω_0, the vibrational frequency. The third term in the brackets accounts, phenomenologically, for vibrational coupling. The presence of such a coupling term gives rise to dispersion of the vibrational frequencies; as shown in reference (17), this dispersion is a vital ingredient of the theory.

Finally $(-J)$ represents the ordinary transfer integral of tight binding theory. As pointed out in reference (16), the case of the small polaron is realized when the electronic bandwidth, $2J$, is small compared to a characteristic energy, $A^2/2M\omega_0^2$, which is the binding energy of the small polaron :

$$2J < A^2/2M\omega_0^2 \quad . \tag{2.4}$$

The above circumstance suggests that equation (2.2) can be solved by a perturbation approach in which the zero'th order Hamiltonian consists of the square bracket of (2.2) whereas the J —proportional term is the perturbation. In zero'th order the electron is trapped at a given site, say the ρ^{th}. The vibrational state is described by a set of vibrational quantum numbers $(\ldots N_k \ldots)$, which give the number of quanta (of frequency ω_k) in each mode. In the presence of the perturbation $(J \neq 0)$, the electron may jump to a neighbouring site $(\rho \rightarrow \rho \mp 1)$ and the vibrational quantum numbers $(\ldots N_k \ldots)$ change to $(\ldots N_{k'} \ldots)$. These transitions can be grouped into two classes:

a) diagonal transitions in which $(\ldots N_k \ldots) = (\ldots N_{k'} \ldots)$

b) non-diagonal transitions in which $(\ldots N_k \ldots) \neq (\ldots N_{k'} \ldots)$

The diagonal transitions dominate at sufficiently low temperatures $T < T_c$, a certain critical temperature defined in reference (17). They give rise to formation of Bloch-type bands whose widths are

$$\Delta E_{\sigma, \ldots N_k \ldots} = 2J\, e^{-S(\ldots N_k \ldots)} \qquad (2.5)$$

which is the product of the electronic bandwidth of the undistorted lattice and a "vibrational overlap integral", the latter being an exponentially decreasing function of temperature. (The estimated value of it at $T = 0$ is about $10^{-2} - 10^{-4}$). So even at the absolute zero of temperature, the polaron bandwidth is very much smaller than the original electronic bandwidth. In this polaron band regime we will normally have non-diagonal transitions as well which act as a perturbation and cause scatterings from one band state to another, determining the life-time of the polaron band

state in the absence of other scattering mechanisms (e.g. impurities).

For $T > T_c \left(\approx \frac{\Theta_0}{2}\right)$, however, the non-diagonal jumps are dominant. In this case, electronic motion is essentially a diffusion process in which the elementary steps are random jumps between neighbouring sites associated with the non-diagonal transitions. If, in addition, the temperature is large compared to the Debye temperature, the quantum mechanical description of the lattice motion goes over into a classical description, the basic physical picture of which may be described as follows: With the electron initially located on the ρ^{th} site, polaron motion occurs principally when the electronic energies of sites (ρ) and $(\rho+1)$ momentarily coincide as a result of the thermal motion of the lattice (i.e. when $-A\chi_\rho = -A\chi_{\rho+1}$). The electron may then hop to the neighbouring site $(\rho \rightarrow \rho \mp 1)$ by virtue of the non-vanishing transfer integral, J. The resulting jump-rate then takes the form of an activation process and reads

$$\omega_T^0 (\rho \rightarrow \rho \mp 1) = \frac{J^2}{\hbar} \left[\frac{\pi}{4kTE_a}\right]^{1/2} e^{-E_a/kT}, \qquad (2.6)$$

where k is the Boltzmann constant, T is the absolute temperature and E_a is the activation energy. This approach is of particular interest for our purposes.

2.2b Binding Energy and Hopping Energy of the Small Polaron:

At the above described classical limit the binding and the hopping energy of the small polaron can be calculated[18] by using a model similar to that of Holstein: Consider two identical molecules 1 and 2 and introduce configurational coordinates X_1 and X_2 in the same way as in Holstein's model. In the absence of the electron the potential energy of the molecules as a function of X will be BX_1^2 and BX_2^2 respectively, where $B = \frac{1}{2} M\omega_o^2$. Let an electron be placed on molecule 1. For a given value of X_1, the interaction energy of the electron will be $-AX_1$. Then the energy of molecule 1 with an extra electron in it will be $BX_1^2 - AX_1$ (Fig. 2.2).

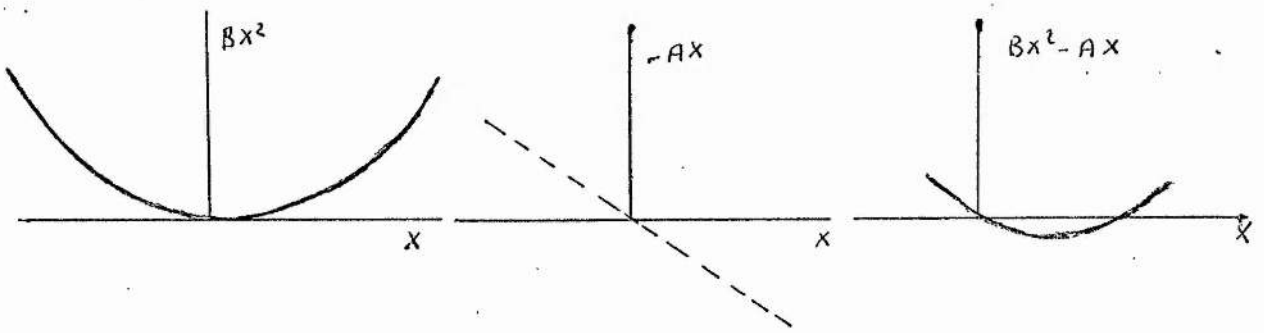

Fig. 2.2. The energy of an electron as a function of a configurational parameter.

Minimization of the above energy gives the polaron-binding energy, W_p:

$$W_p = (BX_1^2 - AX_1)_{min} = \frac{A^2}{4B} = -\frac{A^2}{2M\omega_o^2} \quad . \tag{2.7}$$

If an electron is to jump from one molecule to another, we have seen that the configurational coordinates must be equal, i.e.,

$$X_1 = X_2 = X_c \quad . \tag{2.8}$$

Starting from the condition (2.8) one can calculate the hopping energy which is the minimum energy required for a jump: The energy required to distort molecule 1 and 2 to configurations in which $X_1 = X_2 = X_c$ are $B(X_0 - X_c)^2$ and $B X_c^2$ respectively. So the hopping energy will be

$$W_H = \left[B(X - X_c)^2 + B X_c^2 \right]_{min} = \left[B(X_0 - X_c)^2 + B X_c^2 \right]_{X_c = \frac{X_0}{2}} = \frac{A^2}{4 M \omega_0^2} \quad . \tag{2.9}$$

From (2.7) and (2.9) we note that hopping energy is half the polaron energy:

$$W_H = \frac{1}{2} |W_p| \quad . \tag{2.10}$$

The above considered model corresponds to the case where we have neither random fields in the solid nor an external field. In this case W_H is simply the activation energy, E_a . Otherwise if the energies of an electron on two centres differ by W_D , the activation energy E_a takes the form

$$E_a = W_H + \frac{1}{2} W_D + W_D^2 / 16 W_H \quad . \tag{2.11}$$

2.2c Transport properties of the small polaron of a non-polar crystal in the presence of an applied electric field:

At this stage the theory developed by Friedman[19] applies. In order to apply the previous equation of motion (2.2) to the case of an external field, it must be generalized to three dimensions: i.e., the scalar index n is replaced by a vector index $\underset{\sim}{g}_i = \sum_i g_i \underset{\sim}{a}_i$, where $\underset{\sim}{a}_i$ are a basic set of lattice displacement vectors and g_i are integers. One thus has in place of (2.2)

$$i\hbar \frac{\partial a_{\underset{\sim}{g}}}{\partial t} = \left[H_L - A X_{\underset{\sim}{g}}\right] - \sum_{\underset{\sim}{h}} a_{\underset{\sim}{g}+\underset{\sim}{h}} J_{\underset{\sim}{h}} \quad , \tag{2.12}$$

where H_L stands for the lattice Hamiltonian, $\underset{\sim}{h}$ indexes the nearest neighbours $\underset{\sim}{g}+\underset{\sim}{h}$ of an arbitrary site $\underset{\sim}{g}$, and $J_{\underset{\sim}{h}}$ is defined by

$$J_{\underset{\sim}{h}} = \int dV\, \phi^*(\underset{\sim}{r}-\underset{\sim}{g})\, U(\underset{\sim}{r}-\underset{\sim}{g})\, \phi(\underset{\sim}{r}-\underset{\sim}{g}-\underset{\sim}{h}) \tag{2.13}$$

which corresponds to the transfer integral in three dimensions.

To consider the effect of an applied electric field, $\underset{\sim}{E}_0$, we add the standard electric field term

$$H^{(E)} = e\,\underset{\sim}{E}_0 \cdot \underset{\sim}{r}$$

to the total Hamiltonian. In this process, $H^{(E)}$ automatically separates into two parts. One of these, namely $e\,\underset{\sim}{E}_0 \cdot \underset{\sim}{g}$, appears as an additive modification of the local site energy term $-AX_{\underset{\sim}{g}}$. The other, $e\,\underset{\sim}{E}_0 \cdot (\underset{\sim}{r}-\underset{\sim}{g})$, gets included in the local site Hamiltonian

and results negligible perturbation* on $\phi(\underset{\sim}{r}-\underset{\sim}{g}, x_g)$. Then the equations obeyed by the coefficients reads

$$i\hbar\frac{\partial a_{\underset{\sim}{g}}}{\partial t}=\left[H_L - A x_{\underset{\sim}{g}} + e\underset{\sim}{E}_0\cdot\underset{\sim}{g}\right]a_{\underset{\sim}{g}} - \sum_{\underset{\sim}{h}} a_{\underset{\sim}{g}+\underset{\sim}{h}} J_h \qquad (2.14)$$

and the electric field modified jump rate in the classical limit takes the form

$$\omega_T(\underset{\sim}{g}\to\underset{\sim}{g}')=\omega_T^{(0)}\exp\left[\frac{e\underset{\sim}{E}_0\cdot(\underset{\sim}{g}-\underset{\sim}{g}')}{2kT}\right], \qquad (2.15)$$

where $\omega_T^{(0)}$ is the jump rate in the absence of the applied field which is given by (2.6). It is noted that the effect of the electric field is simply to enhance the jump rate in the field direction.

This summarizes the important features of the small polaron. In the following sections we study the modification of the small polaron theory for the case of a polarizable dielectric and investigate the local field correction to hopping conduction.

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*The local wave-functions are assumed to be nondegenerate, hence can not be affected to first order in the electric field strength.

STUDIES OF SMALL POLARON MOTION FOR A POLARIZABLE DIELECTRIC

2.3a Derivation of the fundamental equation of motion:

In this section, our basic equation of motion is derived. This equation provides the starting point for all subsequent calculations for the case of a polarizable dielectric in the presence of an applied electric field, $\underset{\sim}{E}_0$.

Our physical model is a three-dimensional molecular crystal consisting of N polarizable diatomic molecular sites with fixed centres of gravity and orientation, but with variable internuclear separations.

As previously mentioned, the present method consists of a modification of the usual small polaron formalism. The motion of the electron is formulated in terms of the tight-binding approximation. In the presence of an applied field $\underset{\sim}{E}_0$ the one electron potential may be written as a sum of "molecular" potentials:

$$V(\underset{\sim}{r}, \ldots x_g \ldots) = \sum_g \left[U(\underset{\sim}{r}-\underset{\sim}{g}, x_g) - \frac{e\underset{\sim}{\rho}\cdot(\underset{\sim}{r}-\underset{\sim}{g})}{|\underset{\sim}{r}-\underset{\sim}{g}|^3} \right], \qquad (2.3\text{-}1)$$

where $U(\underset{\sim}{r}-\underset{\sim}{g}, x_g)$ is the short-range contribution of the molecule at site $\underset{\sim}{g}$ and the rest is the long-range contribution due to induced polarization. Here $\underset{\sim}{\rho}$ is the induced dipole moment at lattice site $\underset{\sim}{g}$ and e is the magnitude of the charge of the electron.

In the absence of the applied field $\underset{\sim}{E}_0$ the basic wave functions, $\phi(\underset{\sim}{r}-\underset{\sim}{g}, x_g)$, are assumed to be non-degenerate, hence real, Σ-states, and appropriate to the tight-binding approximation, and are obtained as solutions of the equation

$$\left[-\frac{\hbar^2}{2m}\underset{\sim}{\nabla}^2 + U(\underset{\sim}{r}-\underset{\sim}{q}, x_q) \right] \phi(\underset{\sim}{r}-\underset{\sim}{q}, x_q) = E(x_q)\, \phi(\underset{\sim}{r}-\underset{\sim}{q}, x_q) \tag{2.3-2}$$

with eigenvalues $E(x_q)$ which all depend upon the local internuclear displacement coordinate.

Since the basic wave functions are assumed to be Σ-states, as long as the electric field is not high enough* to cause optical transitions, they satisfy** the following equation as well:

$$\left[-\frac{\hbar^2}{2m}\underset{\sim}{\nabla}^2 + U(\underset{\sim}{r}-\underset{\sim}{q}, x_q) - \frac{e\,\underset{\sim}{p}\cdot(\underset{\sim}{r}-\underset{\sim}{q})}{|\underset{\sim}{r}-\underset{\sim}{q}|^3} + e\,\underset{\sim}{E}_0\cdot(\underset{\sim}{r}-\underset{\sim}{q}) \right] \phi(\underset{\sim}{r}-\underset{\sim}{q}, x_q) = E(x_q)\,\phi(\underset{\sim}{r}-\underset{\sim}{q}, x_q) \tag{2.3-3}$$

The total wave function of the system is represented as a linear superposition of the wave function of the isolated molecules:

$$\Psi(\underset{\sim}{r}, \ldots x_q \ldots) = \sum_{\underset{\sim}{q}} a_q(\ldots x_q \ldots)\, \phi(\underset{\sim}{r}-\underset{\sim}{q}, x_q) \,. \tag{2.3-4}$$

---

*For small polaron the optical transitions start at fields $\approx 10^8$ V cm^{-1} which is far beyond our interest.

**For Σ-states the integral

$$\int |\phi(\underset{\sim}{r}-\underset{\sim}{q}, x_q)|^2 \left[-\frac{e\,\underset{\sim}{p}\cdot(\underset{\sim}{r}-\underset{\sim}{q})}{|\underset{\sim}{r}-\underset{\sim}{q}|^3} + e\,\underset{\sim}{E}_0\cdot(\underset{\sim}{r}-\underset{\sim}{q}) \right] dV$$

vanishes, because $|\phi(\underset{\sim}{r}-\underset{\sim}{q}, x_q)|^2$ is an even function while the square bracket term is odd (see for example, Schiff, L.I., Quantum Mechanics, McGraw-Hill, second edition, p.159, 1965).

Equations for the $a_g(\ldots X_g \ldots)$ are obtained by substitution of (2.3-4) into the Schrödinger equation of the system :

$$i\hbar\frac{\partial\Psi}{\partial t}=\left\{-\frac{\hbar^2}{2m}\nabla^2+\sum_{\underset{\sim}{g}}\left[U(\underset{\sim}{r}-\underset{\sim}{g},X_g)-\frac{e\underset{\sim}{\rho}\cdot(\underset{\sim}{r}-\underset{\sim}{g})}{|\underset{\sim}{r}-\underset{\sim}{g}|^3}\right]+e\underset{\sim}{E}_0\cdot\underset{\sim}{r}\right.$$

$$\left.+\sum_{\underset{\sim}{g}}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial X_g^2}+\frac{1}{2}M\omega_0^2X_g^2\right)\right\}\Psi \qquad (2.3\text{-}5)$$

or

$$i\hbar\frac{\partial\Psi}{\partial t}=\left\{-\frac{\hbar^2}{2m}\nabla^2+U(\underset{\sim}{r}-\underset{\sim}{g}',X_{g'})-\frac{e\underset{\sim}{\rho}\cdot(\underset{\sim}{r}-\underset{\sim}{g}')}{|\underset{\sim}{r}-\underset{\sim}{g}'|^3}+e\underset{\sim}{E}_0\cdot(\underset{\sim}{r}-\underset{\sim}{g}')+e\underset{\sim}{E}_0\cdot\underset{\sim}{g}'\right.$$

$$\left.+\sum_{\underset{\sim}{g}''\neq\underset{\sim}{g}'}\left[U(\underset{\sim}{r}-\underset{\sim}{g}'',X_{g''})-\frac{e\underset{\sim}{\rho}\cdot(\underset{\sim}{r}-\underset{\sim}{g}'')}{|\underset{\sim}{r}-\underset{\sim}{g}''|^3}\right]+\sum_{\underset{\sim}{g}''}\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X_{g''}^2}+\frac{1}{2}M\omega_0^2X_{g''}^2\right)\right\}\Psi. \qquad (2.3\text{-}6)$$

Multiplication on the left with $\phi^*(\underset{\sim}{r}-\underset{\sim}{g},X_g)$ and integration over the electron coordinates, r , gives

$$\sum_{\underset{\sim}{g}'}T_{gg'}\left[i\hbar\frac{\partial}{\partial t}-\sum_{\underset{\sim}{g}''}\left(-\frac{\hbar^2}{2M}\frac{\partial^2}{\partial X_{g''}^2}+\frac{1}{2}M\omega_0^2X_g^2\right)-E(X_{g'})-e\underset{\sim}{E}_0\cdot\underset{\sim}{g}'\right]a_{g'}$$

$$=\sum_{\substack{\underset{\sim}{g}'\\ \underset{\sim}{g}''\neq\underset{\sim}{g}'}}\left[\int\phi(\underset{\sim}{r}-\underset{\sim}{g},X_g)\left[U(\underset{\sim}{r}-\underset{\sim}{g}'',X_{g''})-\frac{e\underset{\sim}{\rho}\cdot(\underset{\sim}{r}-\underset{\sim}{g}'')}{|\underset{\sim}{r}-\underset{\sim}{g}''|^3}\right]\phi(\underset{\sim}{r}-\underset{\sim}{g}',X_{g'})\,dV\right]a_{g'}$$

$$-\frac{\hbar^2}{2M}\sum_{\underset{\sim}{g}'}\int\phi^*(\underset{\sim}{r}-\underset{\sim}{g},X_g)\left[2\frac{\partial\phi(\underset{\sim}{r}-\underset{\sim}{g}',X_{g'})}{\partial X_{g'}}\frac{\partial a_{g'}}{\partial X_{g'}}+a_{g'}\frac{\partial^2\phi(\underset{\sim}{r}-\underset{\sim}{g}',X_{g'})}{\partial^2X_{g'}^2}\right]dV\,, \qquad (2.3\text{-}7)$$

where $E(\chi_{g'})$ is the solution of the equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\underset{\sim}{r}-\underset{\sim}{g}',\chi_{g'}) + e\underset{\sim}{E}_0\cdot(\underset{\sim}{r}-\underset{\sim}{g}') - \frac{e\underset{\sim}{P}\cdot(\underset{\sim}{r}-\underset{\sim}{g}')}{|\underset{\sim}{r}-\underset{\sim}{g}'|^3}\right]\phi(\underset{\sim}{r}-\underset{\sim}{g}',\chi_{g'})$$

$$= E(\chi_{g'})\,\phi(\underset{\sim}{r}-\underset{\sim}{g}',\chi_{g'}), \qquad (2.3\text{-}8)$$

and $T_{\underset{\sim}{g}\underset{\sim}{g}'}$ is

$$T_{gg'} = \int \phi^*(\underset{\sim}{r}-\underset{\sim}{g},\chi_g)\,\phi(\underset{\sim}{r}-\underset{\sim}{g}',\chi_{g'})\,dV = \delta_{gg'} + S_{gg'} \quad . \qquad (2.3\text{-}9)$$

The $S_{gg'}$ are well-known non-orthogonality integrals which will be assumed to differ from zero only for nearest neighbours and to be small compared to unity.

To proceed further we multiply (2.3-6) by the matrix $\breve{T}_{gg'}$ which is the inverse of $T_{gg'}$ as defined by the relation

$$\sum_{\underset{\sim}{g}''} \breve{T}_{gg''}T_{g''g'} = \delta_{gg'} \quad . \qquad (2.3\text{-}10)$$

To first order in the $S_{gg'}$, it is given by the expression

$$\breve{T}_{gg'} = \delta_{gg'} - S_{gg'} + \cdots \quad . \qquad (2.3\text{-}11)$$

One then obtains in place of (2.3-7)

$$\left[i\hbar \frac{\partial}{\partial t} - \sum_{\underset{\sim}{q''}} \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial X_{q''}^2} + \frac{1}{2} M \omega_0^2 X_{q''}^2 \right) - E(X_q) - e \underset{\sim}{E}_0 \cdot \underset{\sim}{q} \right] a_q =$$

$$\sum_{\substack{\underset{\sim}{q'''}, \underset{\sim}{q'} \\ \underset{\sim}{q'''} \neq \underset{\sim}{q'}}} \breve{T}_{qq'''} \left\{ \int \phi(\underset{\sim}{r} - \underset{\sim}{q'''}; X_{q'''}) \left[U(\underset{\sim}{r} - \underset{\sim}{q'''}; X_{q'''}) - \frac{e \underset{\sim}{\rho} \cdot (\underset{\sim}{r} - \underset{\sim}{q'''})}{|\underset{\sim}{r} - \underset{\sim}{q'''}|^3} \right] \phi(\underset{\sim}{r} - \underset{\sim}{q'}; X_{q'}) \, dV \right\} a_{q'}$$

$$- \frac{\hbar^2}{2M} \sum_{\underset{\sim}{q'''}, \underset{\sim}{q'}} \breve{T}_{qq'''} \int \phi(\underset{\sim}{r} - \underset{\sim}{q'''}; X_{q'''}) \left[2 \frac{\partial \phi(\underset{\sim}{r} - \underset{\sim}{q'}; X_{q'})}{\partial X_{q'}} \frac{\partial a_{q'}}{\partial X_{q'}} + \frac{\partial^2 \phi(\underset{\sim}{r} - \underset{\sim}{q'}; X_{q'})}{\partial X_{q'}^2} a_{q'} \right] dV .$$

(2.3-12)

The second term on the right-hand side of (2.3-12) is now dropped. This is justified by the fact that it involves derivatives of electronic wave functions with respect to nuclear coordinates. Such terms essentially represent the effect of the nuclear kinetic energy on the electronic wave functions and are assumed to be small.

We can simplify (2.3-12) further by introducing the assumption of tight-binding approximation. The principal assumption is that of smallness of overlap integrals (integrals involving electron wave functions localized at different sites). These integrals are of two types:

1) non-orthogonality integrals as given by $S_{qq'}$

2) those terms on the right-hand side of (2.3-12) for which $\underset{\sim}{q'} \neq \underset{\sim}{q'''}$:

$$\int \phi(\underset{\sim}{r} - \underset{\sim}{q'''}; X_{q'''}) \left[U(\underset{\sim}{r} - \underset{\sim}{q'''}; X_{q'''}) - \frac{e \underset{\sim}{\rho} \cdot (\underset{\sim}{r} - \underset{\sim}{q'''})}{|\underset{\sim}{r} - \underset{\sim}{q'''}|^3} \right] \phi(\underset{\sim}{r} - \underset{\sim}{q'}; X_{q'}) \, dV .$$

In line with the above assumption, all terms containing products of more than one such overlap integral will be discarded. So the first sum on the right-hand side of (2.3-12) becomes

$$\sum_{\underset{\sim}{g}''\neq\underset{\sim}{g}'}\left\{\int\phi^*(\underset{\sim}{r}-\underset{\sim}{g}',x_{g'})\left[U(\underset{\sim}{r}-\underset{\sim}{g}'',x_{g''})-\frac{e\underset{\sim}{p}\cdot(\underset{\sim}{r}-\underset{\sim}{g}'')}{|\underset{\sim}{r}-\underset{\sim}{g}''|^3}\right]\phi(\underset{\sim}{r}-\underset{\sim}{g}'',x_{g''})\,dV\right\}a_{g''}$$

$$\sum_{\underset{\sim}{g}''\neq\underset{\sim}{g}'}S_{g''g'}\left\{\int\phi^*(\underset{\sim}{r}-\underset{\sim}{g}',x_{g'})\left[U(\underset{\sim}{r}-\underset{\sim}{g}'',x_{g''})-\frac{e\underset{\sim}{p}\cdot(\underset{\sim}{r}-\underset{\sim}{g}'')}{|\underset{\sim}{r}-\underset{\sim}{g}''|^3}\right]\phi(\underset{\sim}{r}-\underset{\sim}{g}'',x_{g''})\,dV\right\}a_{g''}. \tag{2.3-13}$$

At this stage we may employ one more assumption, also appropriate to the case of tight-binding which involves the local character of the molecular potential $U(\underset{\sim}{r}-\underset{\sim}{g}'',x_{g''})$. It will be assumed that those terms in (2.3-13) which contain products of wave functions and potentials localized at different sites are an order of magnitude smaller than terms for which two (or more) such factors refer to the same site*. It then follows that (2.3-13) may be approximated by

$$\sum_{\underset{\sim}{g}''\neq\underset{\sim}{g}}\left[\int\phi^*(\underset{\sim}{r}-\underset{\sim}{g},x_g)\,U(\underset{\sim}{r}-\underset{\sim}{g},x_g)\,\phi(\underset{\sim}{r}-\underset{\sim}{g}',x_{g'})\right]a_{g'}$$

$$+\left[\int|\phi(\underset{\sim}{r}-\underset{\sim}{g},x_g)|^2\sum_{\underset{\sim}{g}''\neq\underset{\sim}{g}}U(\underset{\sim}{r}-\underset{\sim}{g}'',x_{g''})\,dV\right]a_g$$

---

*This argument cannot be applied to the dipolar potential since it has long-ranged character.

$$+\sum_{\underset{\sim}{g}(\neq\underset{\sim}{g})}\left[\int\phi(\underset{\sim}{r}-\underset{\sim}{g},x_g)\left(-\frac{e\underset{\sim}{f}\cdot(\underset{\sim}{r}-\underset{\sim}{g})}{|\underset{\sim}{r}-\underset{\sim}{g}|^3}\right)\phi(r-g',x_{g'})\,dV\right]a_{g'}$$

$$+\left[\int|\phi(\underset{\sim}{r}-\underset{\sim}{g},x_g)|^2\sum_{\underset{\sim}{g}''\neq\underset{\sim}{g}}\left(-\frac{e\underset{\sim}{f}\cdot(\underset{\sim}{r}-\underset{\sim}{g}'')}{|\underset{\sim}{r}-\underset{\sim}{g}''|^3}\right)dV\right]a_g$$

$$+\sum_{\underset{\sim}{g}(\neq\underset{\sim}{g})}\left[\int\phi^*(\underset{\sim}{r}-\underset{\sim}{g},x_g)\sum_{\underset{\sim}{g}''(\neq\underset{\sim}{g},\underset{\sim}{g}')}\left(-\frac{e\underset{\sim}{f}\cdot(\underset{\sim}{r}-\underset{\sim}{g}'')}{|\underset{\sim}{r}-\underset{\sim}{g}''|^3}\right)\phi(\underset{\sim}{r}-\underset{\sim}{g}',x_{g'})\,dV\right]a_{g'}$$

$$-\sum_{\underset{\sim}{g}'}S_{gg'}\left\{\int|\phi(\underset{\sim}{r}-\underset{\sim}{g}',x_{g'})|^2\sum_{g''(\neq g')}\left(-\frac{e\underset{\sim}{f}\cdot(\underset{\sim}{r}-\underset{\sim}{g}'')}{|\underset{\sim}{r}-\underset{\sim}{g}''|^3}\right)dV\right\}a_{g'}$$

$$=\sum_{\underset{\sim}{g}'(\neq\underset{\sim}{g})}J(x_g,x_{g'})a_{g'}+\sum_{\underset{\sim}{g}'(\neq\underset{\sim}{g})}J^f(x_g,x_{g'})a_{g'}+(W_g+W_g^f)a_g-\sum_{g'(\neq g)}S_{gg'}W_{g'}^f a_{g'}\,,$$

(2.3-14)

where

$$J(x_g,x_{g'})=\int\phi^*(\underset{\sim}{r}-\underset{\sim}{g},x_g)\,U(\underset{\sim}{r}-\underset{\sim}{g},x_g)\,\phi(\underset{\sim}{r}-\underset{\sim}{g}',x_{g'})\,dV\,,$$

(2.3-15)

$$J^f(x_g,x_{g'})=\int\phi^*(\underset{\sim}{r}-\underset{\sim}{g},x_g)\sum_{\underset{\sim}{g}''(\neq\underset{\sim}{g})}\left(-\frac{e\underset{\sim}{f}\cdot(\underset{\sim}{r}-\underset{\sim}{g}'')}{|\underset{\sim}{r}-\underset{\sim}{g}''|^3}\right)\phi(\underset{\sim}{r}-\underset{\sim}{g}',x_{g'})\,dV\,,$$

(2.3-16)

$$W_g = \int |\phi(\underset{\sim}{r}-\underset{\sim}{g}, x_g)|^2 \sum_{\underset{\sim}{g}' \neq \underset{\sim}{g}} U(\underset{\sim}{r}-\underset{\sim}{g}', x_{g'})\, dV \quad , \tag{2.3-17}$$

$$W_g^{\rho} = \int |\phi(\underset{\sim}{r}-\underset{\sim}{g}, x_g)|^2 \sum_{\underset{\sim}{g}' \neq \underset{\sim}{g}} \left(- \frac{e\underset{\sim}{\rho}\cdot(\underset{\sim}{r}-\underset{\sim}{g}')}{|\underset{\sim}{r}-\underset{\sim}{g}'|^3} \right) dV \quad . \tag{2.3-18}$$

Substituting (2.3-14) into (2.3-12) and assuming $J(x_g, x_{g'})$, $J^{\rho}(x_g, x_{g'})$ and $S_{gg'}$ are appreciable only for nearest neighbours $\underset{\sim}{g}$ and $\underset{\sim}{g}+\underset{\sim}{h}$ we can write

$$\left[i\hbar \frac{\partial}{\partial t} - \sum_{\underset{\sim}{g}} \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial x_{g\sim}^2} + \frac{1}{2} M\omega_0^2 x_{g\sim}^2 \right) - E(x_g) - e\underset{\sim}{E}_0 \cdot \underset{\sim}{g} - W_g - W_g^{\rho} \right] a_g$$

$$= \sum_{\underset{\sim}{h}} \left[J(x_g, x_{g+h}) + J^{\rho}(x_g, x_{g+h}) - S_{g,g+h} W_{g+h}^{\rho} \right] a_{g+h} \quad . \tag{2.3-19}$$

As discussed in reference (16) we can introduce the following simplifications:

a) Neglect of the energy terms, W_g, because of the fact that $U(\underset{\sim}{r}-\underset{\sim}{g}, x_g)$ is a short-range potential. For a periodic crystal, W_g becomes a constant for each site and is just an additive constant. Therefore it can always be eliminated in (2.3-19) by shifting the zero of energy by the amount of W_g.

b) Neglect of the x_g dependence of the $J(x_g, x_{g+h})$, this is to say the $J(x_g, g+h)$ are all to be taken equal to a single constant, $(-J)$:

$$J(x_g, x_{g+h}) = -J \quad ,$$

where J is positive.

c) The X_g -dependence of $E(X_g)$ is taken to be linear, i.e.,

$$E(X_g) = -AX_g .$$

Here it may be remarked that (b) and (c) in essence are based on the assumption that the electron-lattice interactions have entirely a local character.

d) Further, in Appendix 2A we demonstrate that at fields which we are interested in, the term $\left(J^{\rho}(X_g, X_{g+h}) - S_{g,g+h} W^{\rho}_{g+h} \right)$ becomes very much smaller than $J(X_g, X_{g+h})$, and hence can be neglected. This assumption does not disturb the theory, because as far as the small polaron theory is concerned the overlap term is just a phenomenological quantity whose relative order of magnitude is of importance rather than its calculation in detail.

With the simplification discussed above (2.3-19) reduces to

$$i\hbar \frac{\partial a_g}{\partial t} = \left[H_L - AX_g + e\underset{\sim}{E_0}\cdot\underset{\sim}{g} + W^{\rho}_g \right] a_g - J \sum_{\underset{\sim}{h}} a_{\underset{\sim}{g}+\underset{\sim}{h}} \quad . \qquad (2.3\text{-}20)$$

Equation (2.3-20) will form the basis for study of the small polaron of a polarizable dielectric in the presence of an applied electric field.

It may here be remarked that the only difference between (2.3-20) and (2.14) is the extra W^{ρ}_g term in the square bracket. This term normally varies from point to point. Because the dipole potentials appearing in W^{ρ}_g expression are long-ranged, W^{ρ}_g will depend on $\underset{\sim}{g}$ for a finite crystal. Therefore W^{ρ}_g cannot be eliminated from (2.3-20) by shifting the zero of energy by the amount of W^{ρ}_g . The appearance of this new term in the electronic Hamiltonian gives rise to the possibility of local field

type corrections in the small polaron motion.

As was mentioned in section (2.2a), for temperatures above the Debye temperature the small polaron motion occurs by means of thermally activated hopping between neighbouring sites. It is for this site-jump regime that we investigate the local field type corrections in the small polaron motion. In the following section we calculate the elementary electric field modified jump rate for a polarizable dielectric with a classical occurrence-probability treatment which applies for high temperatures.

FIELD MODIFIED JUMP RATE FOR A POLARIZABLE DIELECTRIC

2.3b Classical occurrence-probability approach:

In this section we calculate the electric field modified jump rate for a polarizable dielectric at high temperatures $(T \gg \Theta_D)$. The electric field modified jump rates have already been calculated in reference (19) for a non-polar crystal. The purpose of the present section is to extend the treatment to the polarizable dielectric. The basis of this treatment is the set of equations

$$i\hbar \frac{\partial a_g}{\partial t} = \left\{ -AX_g(t) + e\underset{\sim}{E}_0 \cdot \underset{\sim}{g} + W_g^{\rho} \right\} a_g - J \sum_b a_{g+h} \qquad (2.3\text{-}21)$$

which is obtained from (2.3-20) by omitting the vibrational Hamiltonian, H_L . This omission is based on the fact that the lattice vibrations are not treated quantum mechanically, but, rather, the $X_g(t)$ are regarded classically as given functions of time. In the classical occurrence probability approach the $X_g(t)$ are determined by the Hamiltonian

$$H_{(initial)} = H_L - AX_{(initial)} \qquad (2.3\text{-}22)$$

i.e. the sum of the purely vibrational Hamiltonian and interaction Hamiltonian before making the transition to a neighbouring site.

Following the argument of reference (19), it will be convenient to drop the electric field terms from (2.3-21). It can be reinserted any time by adding it to the electronic energy as follows:

$$-AX_g \longrightarrow -AX_g + e\underset{\sim}{E}_0 \cdot \underset{\sim}{g} + W_g^{\rho} \,. \qquad (2.3\text{-}23)$$

Consider two neighbouring sites, $\underset{\sim}{g}$ and $\underset{\sim}{g}'$. Assume that at some initial time, t_i , the electron is in site $\underset{\sim}{g}$. Because of the overlap, J , at some $t > t_i$ the electron may be found at $\underset{\sim}{g}'$. The equation for the coefficient $a_{g'}$ will be

$$i\hbar \frac{\partial a_{g'}}{\partial t} = -A X_{g'}(t)\, a_{g'} - J a_g \,. \tag{2.3-24}$$

Following the perturbation theory, to first order, we can write:

$$a_{g'} = \left(\frac{J}{i\hbar}\right) \exp\left[\frac{iA}{\hbar}\int^{t} X_{g'}(t')\,dt'\right] \int_{t_i}^{t} \exp\left\{\frac{iA}{\hbar}\int_{0}^{t'} \left[X_g(t'') - X_{g'}(t'')\right] dt''\right\} dt' \,. \tag{2.3-25}$$

The present classical treatment, as discussed in reference (17), is based on the fact that over the region of interest we have the conditions*

$$kT \gg \hbar\omega_o \,, \tag{2.3-26}$$

$$A^2/M\omega_o^2 \gg \hbar\omega_o \,. \tag{2.3-27}$$

It then follows that the oscillations in the exponential integrand will interfere destructively except at a coincidence point, t_c ; at which $X_{g'}(t_c) = X_g(t_c)$ and at which the phase of the exponential is momentarily stationary.

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*The first inequality simply represents the regime in which the lattice motion can be treated classically, the second insures that the phase undergoes many oscillations between successive coincidence

Further, as in reference (17) we assume that the time variation of $[X_g(t) - X_{g'}(t)]$ is linear in the neighbourhood of t_c :

$$X_g(t) - X_{g'}(t) = (v_g - v_{g'})(t - t_c), \tag{2.3-28}$$

where the classical velocities v_g and $v_{g'}$ are evaluated at t_c .

Inserting (2.3-28) into (2.3-25) and choosing the lower limit of the phase integral to be t_c , one has

$$a_{g'}(t) = \left(-\frac{J}{i\hbar}\right) \exp\left[\frac{iA}{\hbar}\int_{t_c}^{t} X_{g'}(t')\,dt'\right]\int_{t_i}^{t} \exp\left\{\frac{i}{2}\left[\frac{A(v_g - v_{g'})}{\hbar}\right](t' - t_c)^2\right\} dt' \tag{2.3-29}$$

It is also noticed that important contributions to the integral occur over a time integral

$$\Delta t \sim \left[\frac{\hbar}{A(v_g - v_{g'})}\right]^{1/2} \sim \left[\frac{\hbar}{A(kT/M)^{1/2}}\right]^{1/2} = \left[\frac{1}{\omega_0^2}\frac{\hbar\omega_0}{(A^2/M\omega_0^2)^{1/2}(kT)^{1/2}}\right]^{1/2} \ll \frac{1}{\omega_0} \tag{2.3-30}$$

Since the spacing in time between successive coincidence points $(\approx \omega_0^{-1})$ is assumed large compared to Δt , the contributions of different coincidence points will not overlap. One may then replace the integration limits t and t_i by plus and minus infinity respectively, so that

$$a_{g'}(t) = \left(-\frac{J}{i\hbar}\right) \exp\left[\frac{iA}{\hbar}\int_{t_c}^{t} X_{g'}(t')\,dt'\right]\int_{-\infty}^{\infty} \exp\left\{\frac{i}{2}\left[\frac{A(v_g - v_{g'})}{\hbar}\right](t - t_c)^2\right\} dt'$$

$$= \left(-\frac{J}{i\hbar}\right) \exp\left[\frac{iA}{\hbar}\int_{t_c}^{t} X_{g'}(t')\,dt'\right] e^{-i\frac{\pi}{4}} \left(\frac{2\pi\hbar}{A|v_g - v_{g'}|}\right)^{1/2} \tag{2.3-31}$$

To go from occupation amplitudes to occupation probabilities, we take the absolute square of $a_{g'}(t)$:

$$W_c(\underset{\sim}{g}\to\underset{\sim}{g}') = |a_{g'}(t)|^2 = \frac{2\pi J^2}{\hbar}\frac{1}{A|v_g - v_{g'}|}\,, \qquad (2.3\text{-}32)$$

where $W_c(\underset{\sim}{g}\to\underset{\sim}{g}')$ represents the probability of a site jump, $\underset{\sim}{g}\to\underset{\sim}{g}'$, occurring in a single coincidence event.

In order to obtain the transition probability, $\omega_T(\underset{\sim}{g}\to\underset{\sim}{g}')$, giving the average site jump probability per second, equation (2.3-32) is multiplied by the probability per second $P_T^{(c)}(v_r)\,dv_r$, for a coincidence in which the relative velocity, $v_r = v_g - v_{g'}$, lies within a given differential range and integrated over all values of v_r , as in reference (17).

The classical occurrence-probability of such a configuration is given by

$$P_T^{(c)}(v_r)\,dv_r\,dt = Z^{-1}\int\cdots\int dx_1\cdots dx_N\,dv_1\cdots dv_N\; e^{-(H_L - Ax_g)/kT}$$

$$\times\quad \delta(x_g - x_{g'})\,v_r\,dt\,\delta(v_g - v_{g'} - v_r)\,dv_r\,, \qquad (2.3\text{-}33)$$

where

$$Z \equiv \int\cdots\int dx_1\cdots dx_N\,dv_1\cdots dv_N\; e^{-(H_L - Ax_g)/kT} \qquad (2.3\text{-}34)$$

is the total partition function.

Then upon carrying out the velocity integrations and dividing

by dt to obtain the occurrence probability per unit time, one has

$$P_T^{(c)} d\upsilon_r = \left(\frac{M}{4\pi kT}\right)^{1/2} d\upsilon_r \; e^{-M\upsilon_r^2/4kT} \; |\upsilon_r| \, F \; , \qquad (2.3\text{-}35)$$

where

$$F = \frac{\int\cdots\int e^{-(V_L - A\chi_p)/kT} \, \delta(\chi_g - \chi_{g'}) \, d\chi_1 \cdots d\chi_N}{\int\cdots\int e^{-(V_L - A\chi_g)/kT} \, d\chi_1 \cdots d\chi_N} \; ; \qquad (2.3\text{-}36)$$

V_L representing the vibrational potential energy of the host crystal:

$$V_L = \frac{1}{2} M\omega_0^2 \sum_{m=1}^{N} \chi_m^2 \; .$$

To calculate the field modified jump rate for a polarizable crystal, we assume that the electric field and its induced effects enter into occurrence probability in that one looks for coincidence of the electronic plus electric field energies of neighbouring sites. Therefore in (2.3-36) we replace :

$$\delta(\chi_g - \chi_{g'}) \quad \text{by} \quad \delta\left\{\chi_g - \chi_{g'} - \frac{e\,\underset{\sim}{E}_0 \cdot (\underset{\sim}{g} - \underset{\sim}{g}') + (W_g^f - W_{g'}^f)}{A}\right\}$$

or $\delta\left(\chi_g - \chi_{g'} - \frac{\Delta}{A}\right)$ which results from (2.3-23), here

$$\Delta = e\,\underset{\sim}{E}_0 \cdot (\underset{\sim}{g} - \underset{\sim}{g}') + (W_g^f - W_{g'}^f) \qquad (2.3\text{-}37)$$

is the enhancement of the difference of electronic energies at site $\underset{\sim}{q}$ and $\underset{\sim}{q'}$ in the presence of an applied electronic field.

So the field modified F becomes

$$F = \frac{\int\cdots\int e^{-\left(\frac{1}{2}M\omega_0^2\sum_{m=1}^{N}X_m^2 - AX_q\right)/kT}\,\delta\left(X_q - X_{q'} - \Delta/A\right)\,dX_1\cdots dX_N}{\int\cdots\int e^{-\left(\frac{1}{2}M\omega_0^2\sum_{m=1}^{N}X_m^2 - AX_q\right)/kT}\,dX_1\cdots dX_N}$$

$$= \frac{\int dX_1\, e^{-\beta\frac{1}{2}M\omega_0^2X_1^2}\cdots\int dX_q\, e^{-\beta\left[\frac{1}{2}M\omega_0^2X_q^2 - AX_q\right]}\int dX_{q'}\, e^{-\beta\frac{1}{2}M\omega_0^2X_{q'}^2}\,\delta(X_q - X_{q'} - \Delta/A)\cdots\int dX_N\, e^{-\beta\frac{1}{2}M\omega_0^2X_N^2}}{\int dX_1\, e^{-\beta\frac{1}{2}M\omega_0^2X_1^2}\cdots\int dX_q\, e^{-\beta\left[\frac{1}{2}M\omega_0^2X_q^2 - AX_q\right]}\int dX_{q'}\, e^{-\beta\frac{1}{2}M\omega_0^2X_{q'}^2}\cdots\int dX_N\, e^{-\beta\frac{1}{2}M\omega_0^2X_N^2}}$$

$$= \frac{\int dX_1\, e^{-\beta\frac{1}{2}M\omega_0^2X_1^2}\cdots\int dX_q\, e^{-\beta\left\{\frac{1}{2}M\omega_0^2\left[X_q^2 + \left(X_q - \frac{\Delta}{A}\right)^2\right] - AX_q\right\}}\cdots\int dX_N\, e^{-\beta\frac{1}{2}M\omega_0^2X_N^2}}{\int dX_1\, e^{-\beta\frac{1}{2}M\omega_0^2X_1^2}\cdots\int dX_q\, e^{-\beta\left[\frac{1}{2}M\omega_0^2X_q^2 - AX_q\right]}\int dX_{q'}\, e^{-\beta\frac{1}{2}M\omega_0^2X_{q'}^2}\cdots\int dX_N\, e^{-\beta\frac{1}{2}M\omega_0^2X_N^2}} \qquad (2.3\text{-}38)$$

Carrying out the integrations in the nominator and denominator of (2.3-38) one has

$$F = \frac{A}{2R}\left(\frac{R}{4kTE_a}\right)^{1/2} e^{-E_a/kT}\, e^{\beta\left[\frac{\Delta}{2} - \frac{1}{16}\frac{\Delta^2}{E_a}\right]} \qquad (2.3\text{-}39)$$

which when inserted into (2.3-35) yields

$$P_T^{(c)} d\upsilon_r = \left(\frac{M}{4\pi kT}\right) d\upsilon_r \, e^{-M\upsilon_r^2/4kT} \, |\upsilon_r| \, \frac{A}{2\pi} \left(\frac{\pi}{4kTE_a}\right) e^{-E_a/kT} \, e^{\left(\frac{\Delta}{2} - \frac{\Delta^2}{16E_a}\right)/kT} \,. \tag{2.3-40}$$

Multiplying (2.3-40) by (2.3-30), and integrating over all $\upsilon_r = \upsilon_q - \upsilon_{q'}$ we obtain the transition probability (jump rate);

$$\omega_T(\underset{\sim}{q} \to \underset{\sim}{q}') = \frac{J^2}{h} \left(\frac{\pi}{4kTE_a}\right)^{1/2} e^{-E_a/kT} \, e^{\left(\frac{\Delta}{2} - \frac{\Delta^2}{16E_a}\right)/kT} \,. \tag{2.3-41}$$

Comparing (2.3-41) with (2.6) we can write the field modified jump rate, $\omega_T(\underset{\sim}{q} \to \underset{\sim}{q}')$:

$$\omega_T(\underset{\sim}{q} \to \underset{\sim}{q}') = \omega_T^{\circ}(q \to q') \, e^{\left(\frac{\Delta}{2} - \frac{\Delta^2}{16E_a}\right)/kT} \,. \tag{2.3-42}$$

Equation (2.3-42) predicts a peak at $\Delta = 4E_a$ which corresponds to fields $\approx 10^8$ V cm^{-1} (see reference 20). Therefore for fields up to 10^6 V cm^{-1} the effect of the Δ^2 term in (2.3-42) can be neglected, and substituting the value of Δ from (2.3-37) it takes the form

$$\omega_T(\underset{\sim}{q} \to \underset{\sim}{q}') = \omega_T^{\circ}(\underset{\sim}{q} \to \underset{\sim}{q}') \, e^{\left[e\underset{\sim}{E}_o \cdot (\underset{\sim}{q} - \underset{\sim}{q}') + (W_q^f - W_{q'}^f)\right]/2kT} \,. \tag{2.3-43}$$

It is noted that, for the case of a polarizable dielectric, the net electric field appearing in the jump rate might be different from the applied electric field, E_o . The reason for this is

the extra $(W_g^p - W_g^{p'})$ term in the exponential part. This term gives rise to the possibility of the local field correction to hopping probability, and hence to hopping conductivity.

HOPPING CONDUCTIVITY FOR A POLARIZABLE DIELECTRIC

2.3c Classical approach:

Having calculated the electric field modified jump rate for a polarizable dielectric, at high temperatures $(T \gg \Theta_D)$, it is now our task to calculate the hopping conductivity of a polarizable dielectric. We follow a method similar to one by Efros[13].

Consider a general site $\underset{\sim}{q} = \sum_i q_i \underset{\sim}{a}_i$ and six nearest neighbouring sites $\underset{\sim}{q} \pm \underset{\sim}{a}_i = \underset{\sim}{q} \mp \underset{\sim}{a}_i$. Let f_q be the probability that there is an extra electron at the lattice site $\underset{\sim}{q}$. Then f_q satisfies the following rate equation:

$$\frac{df_q}{dt} = \sum \left\{ \left[\omega_T(\underset{\sim}{q} + q_i \to \underset{\sim}{q}) f_{q+a_i} - \omega_T(\underset{\sim}{q} \to \underset{\sim}{q} + \underset{\sim}{a}_i) f_q \right] \right.$$

$$\left. - \left[\omega_T(\underset{\sim}{q} \to \underset{\sim}{q} - \underset{\sim}{a}_i) f_q - \omega_T(\underset{\sim}{q} - \underset{\sim}{a}_i \to \underset{\sim}{q}) f_{q-a_i} \right] \right\}, \quad (2.3\text{-}44)$$

where $\omega_T(\underset{\sim}{q} \to \underset{\sim}{q} \mp \underset{\sim}{a}_i)$ and $\omega_T(\underset{\sim}{q} \mp \underset{\sim}{a}_i \to \underset{\sim}{q})$ are the jump-rates from $\underset{\sim}{q}$ to $\underset{\sim}{q} \mp \underset{\sim}{a}_i$ and from $\underset{\sim}{q} \mp \underset{\sim}{a}_i$ to $\underset{\sim}{q}$ respectively and given by the expressions (2.3-42) or (2.3-43).

It is noted that all the indices in the second bracket of (2.3-44) differ by a lattice vector $\underset{\sim}{a}_i$ from the corresponding indices in the first bracket and, therefore, assuming that the non-uniformity is small, this difference can be changed to a derivative with respect to x_i :

$$\frac{df_q}{dt} = |a_i| \sum_i \frac{\partial}{\partial x_i} \left[\omega_T(\underset{\sim}{q} + \underset{\sim}{a}_i \to \underset{\sim}{q}) f_{q+a_i} - \omega_T(\underset{\sim}{q} \to \underset{\sim}{q} + \underset{\sim}{a}_i) f_q \right]. \quad (2.3\text{-}45)$$

For this same reason one can substitute $f_g = n/N$ in the left-hand side of (2.3-45), where n is the electron concentration and N is the number of sites per unit volume (which is assumed to be constant). Thus if we multiply (2.3-45) by the electronic charge $(-e)$, we obtain

$$-e\frac{dn}{dt} = -e|a_i| N \sum_i \frac{\partial}{\partial x_i}\left[\omega_T(\underset{\sim}{g}+\underset{\sim}{q}_i \rightarrow \underset{\sim}{g}) f_{g+a_i} - \omega_T(\underset{\sim}{g} \rightarrow \underset{\sim}{g}+\underset{\sim}{q}_i) f_g\right] . \tag{2.3-46}$$

Equation (2.3-46) has the form of a continuity equation and therefore the current J is equal to

$$\underset{\sim}{J} = \sum_i e\, \underset{\sim}{q}_i N\left[\omega_T(\underset{\sim}{g}+\underset{\sim}{q}_i \rightarrow \underset{\sim}{g}) f_{g+a_i} - \omega_T(g \rightarrow g+a_i) f_g\right] . \tag{2.3-47}$$

If we assume that the applied electric field, E_o, is in the q_1 direction (2.3-47) reduces to

$$J = eaN\left[\omega_T(\underset{\sim}{g}+\underset{\sim}{q}_1 \rightarrow \underset{\sim}{g}) f_{g+a_1} - \omega_T(g \rightarrow g+a_1) f_g\right] , \tag{2.3-48}$$

where $J = |\underset{\sim}{J}|$ and $a = |\underset{\sim}{q}_i|$, the lattice spacing.

Further, in the presence of the applied electric field we can write

$$f_{g+a_1} = f_g^o + \frac{a}{2}\frac{\partial f}{\partial x_1} \quad , \quad f_g = f_{g+a_1}^o - \frac{a}{2}\frac{\partial f}{\partial x_1} .$$

with $f_g^\circ = f_{g+a_1}^\circ = \frac{n}{N}$, the equilibrium probabilities,

$$\omega_T(\underset{\sim}{g}+\underset{\sim}{a}_1 \rightarrow \underset{\sim}{g}) = \omega_T^\circ(\underset{\sim}{g}+\underset{\sim}{a}_1 \rightarrow \underset{\sim}{g}) - \frac{\Delta\omega}{2} \quad ,$$

$$\omega_T(\underset{\sim}{g} \rightarrow \underset{\sim}{g}+\underset{\sim}{a}_1) = \omega_T^\circ(\underset{\sim}{g} \rightarrow \underset{\sim}{g}+\underset{\sim}{a}_1) + \frac{\Delta\omega}{2}$$

with $\omega_T^\circ(\underset{\sim}{g}+\underset{\sim}{a}_1 \rightarrow \underset{\sim}{g}) = \omega_T^\circ(\underset{\sim}{g} \rightarrow \underset{\sim}{g}+\underset{\sim}{a}_1)$, the equilibrium jump rates, then (2.3-48) becomes

$$J = e a^2 \omega_T^\circ(g \rightarrow g+a_1) \frac{\partial n}{\partial x_1} + e n a \Delta\omega \quad , \tag{2.3-49}$$

where $\Delta\omega = \omega_T(\underset{\sim}{g} \rightarrow \underset{\sim}{g}+\underset{\sim}{a}_1) - \omega_T(\underset{\sim}{g}+\underset{\sim}{a}_1 \rightarrow \underset{\sim}{g})$.

The first term in (2.3-49) is the usual diffusion current, while the second term is related to the asymmetry of the transition probabilities. If the concentration is uniform the first term can be neglected and substituting the values of $\omega_T(\underset{\sim}{g} \rightarrow \underset{\sim}{g}+\underset{\sim}{a}_1)$ and $\omega_T(\underset{\sim}{g}+\underset{\sim}{a}_1 \rightarrow \underset{\sim}{g})$ from (2.3-43) we obtain

$$J = 2ean\omega_T^\circ(g \rightarrow g+a_1) \sinh\left[\frac{eE_0 \cdot a_1 + (W_{g+a_1}^p - W_g^p)}{2kT}\right] . \tag{2.3-50}$$

Dividing the both sides of (2.3-50) by macroscopic field, E_{mac} , we obtain the hopping conductivity :

$$\sigma(E) = \frac{ean2\omega_T^\circ(g \rightarrow g+a_1)}{E_{mac}} \sinh\left[\frac{eE_0 a + (W_{g+a_1}^p - W_g^p)}{2kT}\right] . \tag{2.3-51}$$

From (2.3-51) it is seen that the problem of investigation of the local field correction to hopping conduction reduces to the evaluation of $(W^{\rho}_{q+a_1} - W^{\rho}_{q})$. This term is calculated in detail in section (2.4). Applying the results we can write,

$$e a E_0 + (W^{\rho}_{q+a_1} - W^{\rho}_{q}) = e a E_0 + e a E_1 = e a E_{mac} \quad . \tag{2.3-52}$$

Substituting (2.3-52) into (2.3-51) we get the hopping conductivity for a polarizable dielectric:

$$\sigma(E) = \sigma(0) \frac{\sinh [e a E_{mac}/2kT]}{[e a E_{mac}/2kT]} \tag{2.3-53}$$

which has no local field correction. Here $\sigma(0)$ is the low field conductivity and given by

$$\sigma(0) = \frac{e^2 a^2 n}{kT} \omega_T^{\circ} (\underset{\sim}{q} \rightarrow \underset{\sim}{q} + \underset{\sim}{q_1}) \quad . \tag{2.3-54}$$

The $\sinh$ function in (2.3-53) implies non-ohmic behaviour when $E_{mac} \gg \frac{kT}{ea}$. For $a \sim 5 A^{\circ}$ and $T = 300K$, non-ohmic behaviour occurs for fields greater than 5×10^5 V cm^{-1}.

INVESTIGATION OF THE LOCAL FIELD CORRECTION TO SMALL POLARON HOPPING CONDUCTION

Before going into detail of this section we note that the result of this section has been published as a short letter[22].

2.4a Introduction:

In section (2.3b) we saw that, in the classical high temperature site jump regime, the jump rate between nearest neighbouring sites $\underset{\sim}{q}$ and $\underset{\sim}{q}''$ is given by

$$\omega_T(\underset{\sim}{q}\to\underset{\sim}{q}'') = \omega_T^{\circ}(\underset{\sim}{q}\to\underset{\sim}{q}'')\exp\left[\frac{eE_0\cdot(\underset{\sim}{q}-\underset{\sim}{q}'')+(W_q^{f}-W_{q''}^{f})}{2kT}\right], \quad (2.4\text{-}1)$$

where $\omega_T^{\circ}(\underset{\sim}{q}\to\underset{\sim}{q}'')$ is the jump rate in the absence of the external electric field. As was pointed out earlier, the possibility for local correction to the jump rate, and hence to the conductivity arises due to the presence of the new term $[W_q^{f}-W_{q''}^{f}]$ in the exponential factor. So the problem reduces to an evaluation of $[W_q^{f}-W_{q''}^{f}]$ for nearest neighbouring sites $\underset{\sim}{q}$ and $\underset{\sim}{q}''$ with W_q^{f} given by

$$W_q^{f} = -e\int d^3r\,|\phi(\underset{\sim}{r}-\underset{\sim}{q})|^2\sum_{\underset{\sim}{q}'\neq\underset{\sim}{q}}\frac{\underset{\sim}{P}\cdot(\underset{\sim}{r}-\underset{\sim}{q}')}{|\underset{\sim}{r}-\underset{\sim}{q}'|^3}\,. \quad (2.4\text{-}2)$$

First it is noted that the question at hand applies equally to the case of point charges and nothing of principle is gained by averaging the dipolar potentials over a finite localized wave function. Hence the latter are taken to be delta functions at the lattice points $\underset{\sim}{q}$ so that from (2.4-2) we obtain:

$$W_q^{f} = -e\sum_{\underset{\sim}{q}'\neq\underset{\sim}{q}}\frac{\underset{\sim}{P}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} \quad (2.4\text{-}3)$$

and

$$-\frac{1}{e}\left[W_{\underset{\sim}{q}}^{p}-W_{\underset{\sim}{q}''}^{p}\right]=\sum_{\underset{\sim}{q}'\neq\underset{\sim}{q}}\frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^{3}}-\sum_{\underset{\sim}{q}'\neq\underset{\sim}{q}''}\frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}''-\underset{\sim}{q}')}{|\underset{\sim}{q}''-\underset{\sim}{q}'|^{3}}\ . \qquad (2.4\text{-}4)$$

The most direct way of evaluating the difference (2.4-4) is to note that for every dipole at $\underset{\sim}{q}'$ which contributes to $W_{\underset{\sim}{q}}^{p}$, there is a corresponding dipole at $\underset{\sim}{q}'+(\underset{\sim}{q}''-\underset{\sim}{q})$ which contributes identically to $W_{\underset{\sim}{q}''}^{p}$. So in taking the difference they cancel. This cancellation occurs in detail until the outer surfaces of the specimen are reached [fig. (2.3)].

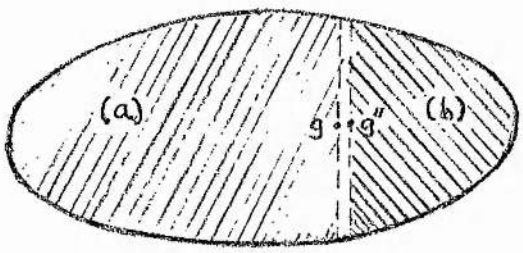


Figure (2.2)

Hence, it is clear that

$$-\frac{1}{e}\left[W_{\underset{\sim}{q}}^{p}-W_{\underset{\sim}{q}''}^{p}\right]=S_{\underset{\sim}{q}}^{(b)}-S_{\underset{\sim}{q}''}^{(a)}\ , \qquad (2.4\text{-}5)$$

where $S_{\underset{\sim}{q}}^{(b)}$ is the contribution to the dipole potential at $\underset{\sim}{q}$ of the surface of dipoles (b), while $S_{\underset{\sim}{q}''}^{(a)}$ is that at $\underset{\sim}{q}''$ due to the dipole surface (a), i.e.

$$S_{\underset{\sim}{q}}^{(b)} = \sum_{\underset{\sim}{q}'} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} \qquad (2.4\text{-}6)$$

(on the surface (b))

and

$$S_{\underset{\sim}{q}''}^{(a)} = \sum_{\underset{\sim}{q}'} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}''-\underset{\sim}{q}')}{|\underset{\sim}{q}''-\underset{\sim}{q}'|^3} \qquad (2.4\text{-}7)$$

(on the surface (a))

In the following sections we will first calculate $[W_{\underset{\sim}{q}}^{p} - W_{\underset{\sim}{q}''}^{p}]$ for samples in the shape of a slab and a sphere then try to find the general expressions for a sample in the shape of a general ellipsoid of revolution.

2.4b Evaluation of $[W_g^p - W_{g''}^p]$ for an infinite slab:

For an infinite slab (2.4-5) becomes

$$-\frac{1}{e}[W_g^p - W_{g''}^p] = S_g^{(b)} - S_{g''}^{(a)} \quad , \qquad (2.4\text{-}8)$$

where $S_g^{(b)}$ is the contribution to the dipole potential at $\underset{\sim}{g}$ of the plane of dipoles (b), while $S_g^{(a)}$ is that at $\underset{\sim}{g}''$ due to the dipole plane (a) [c.f. fig. (2.3)],

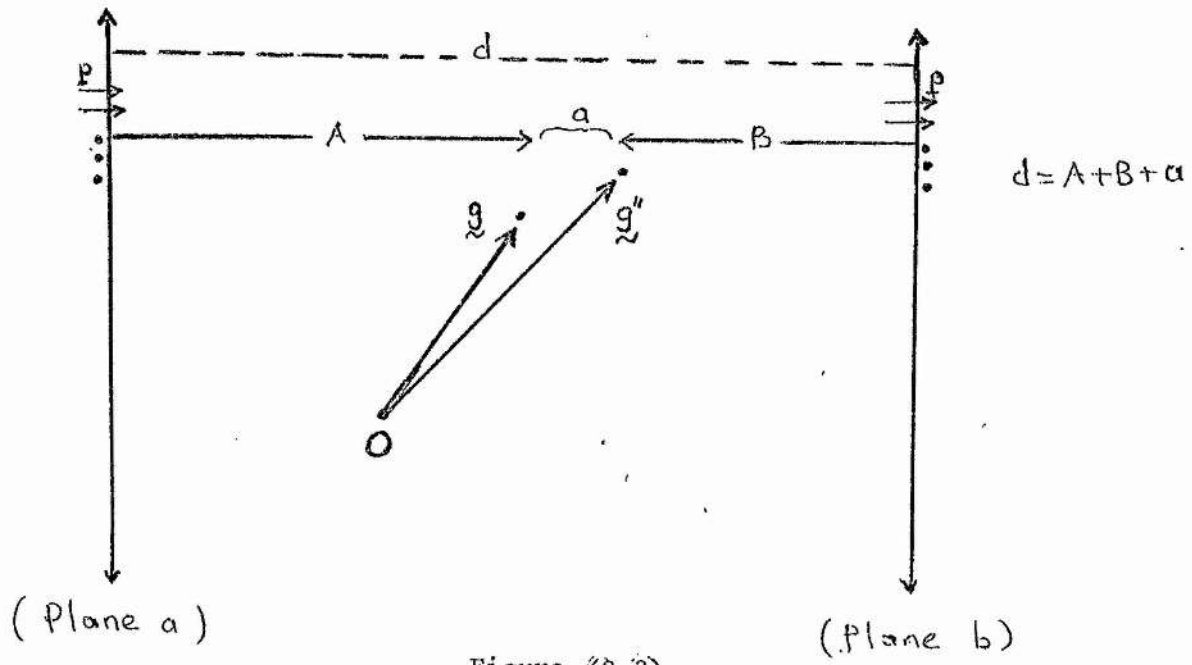


Figure (2.3)

$$S_g^{(b)} = \sum_{\underset{\sim}{g}'} \frac{\underset{\sim}{\rho}\cdot(\underset{\sim}{g}-\underset{\sim}{g}')}{|\underset{\sim}{g}-\underset{\sim}{g}'|^3} \qquad (2.4\text{-}9)$$

[in the plane (b)]

and

$$S_{g''}^{(a)} = \sum_{[g' \text{ in the plane } (a)]} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{g}''-\underset{\sim}{g}')}{|\underset{\sim}{g}''-\underset{\sim}{g}'|^3} \quad . \tag{2.4-10}$$

The plane-wise summation of dipole potentials may be evaluated either by a discrete summation over the respective planes or by approximating the latter by a continuous dipole surface density, this being valid for the majority of pairs of sites $\underset{\sim}{g}$, $\underset{\sim}{g}''$ which are sufficiently distant from the surface of the specimen.

Preliminaries: We will consider lattice sums of perfect simple lattice (Bravais lattice) with cubic symmetry; the usual notation for Bravais lattices will be used. The unit cell of the lattice is specified by the basis vectors $\underset{\sim}{a}_1$, $\underset{\sim}{a}_2$, $\underset{\sim}{a}_3$. The volume of the unit cell is

$$v_a = \underset{\sim}{a}_1 \cdot (\underset{\sim}{a}_2 \times \underset{\sim}{a}_3) \tag{2.4-11}$$

and the unit cell of the reciprocal lattice is mapped out by the reciprocal lattice vectors $\underset{\sim}{b}_1$, $\underset{\sim}{b}_2$, $\underset{\sim}{b}_3$ defined by the relations

$$\underset{\sim}{a}_i \cdot \underset{\sim}{b}_j = \delta_{ij} \quad . \tag{2.4-12}$$

A) Calculation of $S_g^{(b)}$ and $S_{g''}^{(a)}$ by direct summation method:

Assuming that $\underset{\sim}{\mu}$ is perpendicular to the plane [c.f. fig. (2.5)] it is seen that (2.4-9) can be factorized as follows:

$$S_g^{(b)} = -B\rho \sum_{\substack{g' \\ [\text{in the plane } (a)]}} \frac{1}{|\underset{\sim}{g}-\underset{\sim}{g}'|^3} \,, \qquad (2.4\text{-}13)$$

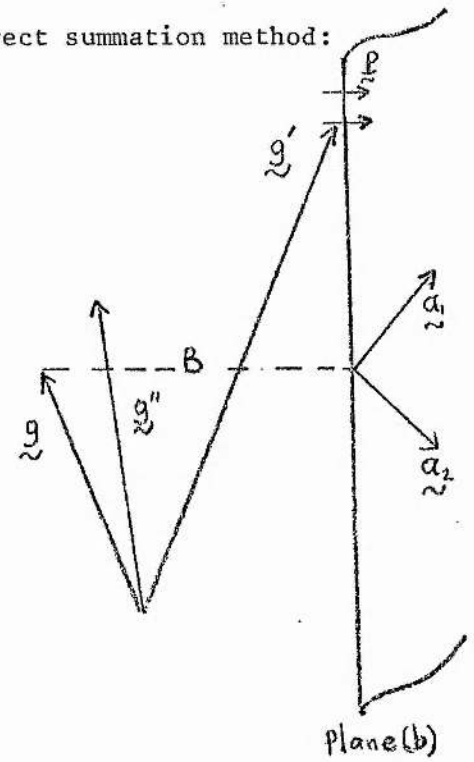


Figure (2.5)

where B is the perpendicular distance between $\underset{\sim}{g}$ and the plane (b) and $\underset{\sim}{\mu}$ is the induced dipole moment and assumed to be parallel to the applied field and is identical for all sites $\underset{\sim}{g}$. Equation (2.4-13) can be written, alternatively, as

$$S_g^{(b)} = -B\rho \sum_{(\lambda_1,\lambda_2)} \frac{1}{|\lambda_1 \underset{\sim}{a}_1 + \lambda_2 \underset{\sim}{a}_2 + \lambda_3 \underset{\sim}{a}_3|^3} \,. \qquad (2.4\text{-}14)$$

Here we denote $\underset{\sim}{g}-\underset{\sim}{g}' = \lambda_1 \underset{\sim}{a}_1 + \lambda_2 \underset{\sim}{a}_2 + \lambda_3 \underset{\sim}{a}_3$, where $\lambda_1, \lambda_2 = 0, \mp 1, \mp 2, \ldots$ and λ_3 is a definite integer. So from figure (2.5) it is seen that $\underset{\sim}{a}_3$ is perpendicular to the plane (b). Introducing the dimensionless quantity $\rho_{\lambda'} = \frac{|\underset{\sim}{g}-\underset{\sim}{g}'|}{a}$, with a being lattice distance, we may write

$$S_g^{(b)} = -\frac{B\rho}{a^3} \sum_{\lambda'} \frac{1}{\rho_{\lambda'}^3} = -B\rho \sum_{\lambda'} \frac{1}{\rho_{\lambda'}^3} \,, \qquad (2.4\text{-}15)$$

where $\lambda' = (\lambda_1, \lambda_2)$ and $\underset{\sim}{P} = \frac{\underset{\sim}{p}}{a^3}$ is the macroscopic polarization.

Choosing the dimensionless basis vector $\underset{\sim}{\alpha}_3 = \frac{\underset{\sim}{a}_3}{a}$ along the Z-axis (which is parallel to $\underset{\sim}{p}$), we may decompose ρ_λ as $\rho_\lambda = (\sigma_{\lambda'}^2 + \lambda_3^2 \alpha_3^2)^{1/2}$, where $\sigma_{\lambda'}$ gives the location of $\underset{\sim}{g}'$ in the plane. So equation (2.4-15) becomes

$$S_g^{(b)} = -BP \sum_{\lambda'} \frac{1}{(\sigma_{\lambda'}^2 + \lambda_3^2 \alpha_3^2)^{3/2}} \qquad (2.4\text{-}16)$$

which can be written as an integral

$$S_g^{(b)} = -BP \int \sum \delta(\underset{\sim}{\sigma} - \underset{\sim}{\sigma}_{\lambda'}) \frac{1}{(\sigma^2 + \lambda_3^2 \alpha_3^2)^{3/2}} d^2\sigma . \qquad (2.4\text{-}17)$$

In Appendix 2B the evaluation of the integral (2.4-17) is carried out by two-dimensional Fourier transform and it is found that

$$S_g^{(b)} = \frac{-2\pi BP}{\lambda_3} \coth(\pi \lambda_3) . \qquad (2.4.18)$$

If we remember that λ_3 is the number of unit cells between the point $\underset{\sim}{g}$ and the plane (b), we can put a superscript (b) to distinguish it from the case for the plane (a). So (2.4-18) becomes

$$S_g^{(b)} = \frac{-2\pi BP}{\lambda_3^{(b)}} \coth[\pi \lambda_3^{(b)}] . \qquad (2.4\text{-}19)$$

With a similar argument we can write

$$S_{g''}^{(a)} = \frac{2\pi A P}{\lambda_3^{(a)}} \coth\left[\pi \lambda_3^{(a)}\right] \quad , \qquad (2.4\text{-}20)$$

where A is the perpendicular distance between the point $\underset{\sim}{g}''$ and the plane (a) . And $\lambda_3^{(a)}$ is the number of unit cells between the point $\underset{\sim}{g}''$ and the plane (a) .

Substituting (2.4-19) and (2.4-20) into (2.4-8) we obtain

$$-\frac{1}{e}\left[W_g^f - W_{g''}^f\right] = -\frac{2\pi B P}{\lambda_3^{(b)}} \coth\left[\pi \lambda_3^{(b)}\right] - \frac{2\pi A P}{\lambda_3^{(a)}} \coth\left[\pi \lambda_3^{(a)}\right]. \qquad (2.4\text{-}21)$$

Now put $B = \lambda_3^{(b)} a$ and $A = \lambda_3^{(a)} a$ into (2.4-21), then we get

$$-\frac{1}{e}\left[W_g^f - W_{g''}^f\right] = -2\pi a P\left[\coth\left(\frac{\pi B}{a}\right) + \coth\left(\frac{\pi A}{a}\right)\right]. \qquad (2.4\text{-}22)$$

Equation (2.4-22) is the exact result of discrete summation for any pair $\underset{\sim}{g}$ and $\underset{\sim}{g}''$. But for the points $\underset{\sim}{g}$ and $\underset{\sim}{g}''$ which are sufficiently distant from the surface of the specimen [i.e. $\frac{B}{a}, \frac{A}{a} \gg 1$], the $\coth$ terms go to unity. So (2.4-22) becomes

$$-\frac{1}{e}\left[W_g^f - W_{g''}^f\right] = -4\pi a P \quad . \qquad (2.4\text{-}23)$$

Remembering the definition of the depolarization field, $\underset{\sim}{E}_1$, for an infinite slab, we can rewrite Eq. (2.4-23) as.

$$-\frac{1}{e}\left[W_g^p - W_{g''}^p\right] = \underset{\sim}{E}_1 \cdot (\underset{\sim}{g}'' - \underset{\sim}{g}) \qquad (2.4\text{-}24)$$

or

$$W_g^p - W_{g''}^p = e\, \underset{\sim}{E}_1 \cdot (\underset{\sim}{g} - \underset{\sim}{g}'') \quad . \qquad (2.4\text{-}25)$$

B) Calculation of $S_g^{(b)}$ and $S_{g''}^{(a)}$ for a slab by continuum approximation:

It has been pointed out that for the points $\underset{\sim}{g}$, $\underset{\sim}{g}''$ which are sufficiently distant from the surface of the specimen, the dipole planes (a) and (b) can be regarded as a continuous dipole surface with surface dipole polarization density $\underset{\sim}{P}_\sigma = a\,\underset{\sim}{P}$ [c.f. fig. (2.6)] where $\underset{\sim}{P}$ is the volume polarization and a is the lattice distance. As we see from fig. (2.6) all dipole elements in a thin ring-shaped segment of a disk lie at the same distance from $\underset{\sim}{g}$. If (s) denotes the radius of such a ring-like segment and ds its width, its area is $dA = 2\pi s\, ds$. The

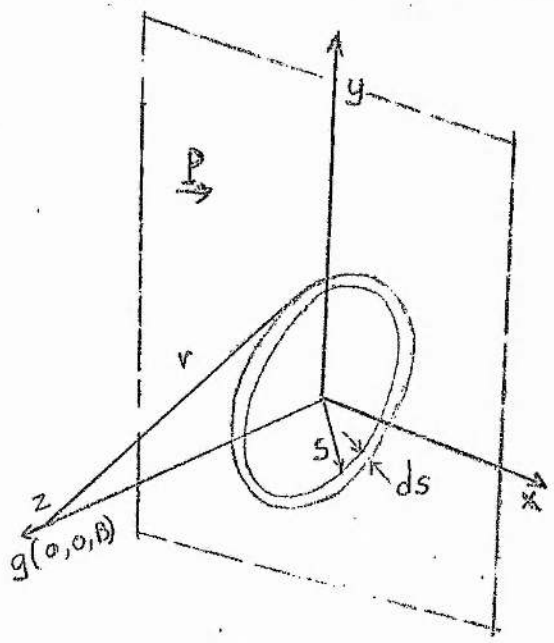


Fig. (2.6)

dipole moment $d\underset{\sim}{P}$ that is contained in dA is therefore $d\underset{\sim}{P} = \underset{\sim}{P}_0\, dA = \underset{\sim}{P}_0\, 2\pi s\, ds = 2\pi a s \underset{\sim}{P} ds$. Thus the contribution of the ring to the potential at $\underset{\sim}{q}$ is $-\frac{d\underset{\sim}{P}\cdot\underset{\sim}{r}}{r^3} = -\frac{B\, dP}{r^3}$, where $r = \sqrt{B^2+s^2}$. To get the potential due to the whole plane (b), $S_q^{(b)}$, we have to integrate over all such rings. So

$$S_q^{(b)} = -\int \frac{d\underset{\sim}{P}\cdot\underset{\sim}{r}}{r^3} = -\int -\frac{B\, dP}{r^3} = -\int_0^\infty \frac{B\, 2\pi a s P\, ds}{(B^2+s^2)^{3/2}}$$

$$= -2\pi a P B \int_0^\infty \frac{s\, ds}{(B^2+s^2)^{3/2}} = -2\pi a P$$

or

$$S_q^{(b)} = -2\pi a P \quad . \tag{2.4-26}$$

By means of a similar argument, we can calculate $S_{q''}^{(a)}$. It is found to be

$$S_{q''}^{(a)} = 2\pi a P \quad . \tag{2.4-27}$$

Substitution of (2.4-26) and (2.4-27) into (2.4-8) gives

$$-\frac{1}{e}\left[W_q^P - W_{q''}^P\right] = -4\pi a P \quad . \tag{2.4-28}$$

Following the arguments given in (2.4-23), we can write

$$W_{\underset{\sim}{q}}^{\rho} - W_{\underset{\sim}{q}''}^{\rho} = e\, \underset{\sim}{E}_1 \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') \quad . \qquad (2.4\text{-}29)$$

The resulting equation (2.4-29) agrees with that of discrete summation (2.4-25) which is valid for points $\underset{\sim}{q}$ and $\underset{\sim}{q}''$ which are sufficiently distant from the surface of the specimen.

2.4c Evaluation of $[W_q^p - W_{q''}^p]$ for a sphere:

Consider the equation (2.4-4), the general expression for $[W_q^p - W_{q''}^p]$;

$$-\frac{1}{e}[W_q^p - W_{q''}^p] = \sum_{q'(\neq q)} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} - \sum_{q'(\neq q'')} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}''-\underset{\sim}{q}')}{|\underset{\sim}{q}''-\underset{\sim}{q}'|^3} \quad (2.4\text{-}30)$$

and construct the fictitious Lorentz sphere concentric with the point O' as is shown in fig. (2.7) (O' is the point, equidistant from $\underset{\sim}{q}$ and $\underset{\sim}{q}''$). The radius, R of the sphere must be chosen sufficiently large that we can make continuum approximation outside it. So the above summation can be split into two parts:

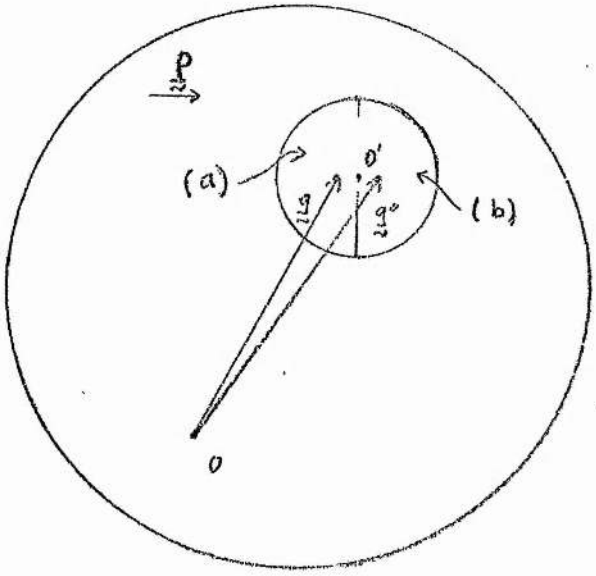


Figure (2.7).

a) Summation individually over the dipoles inside the Lorentz sphere

b) Contribution from the outside dipoles,

$$-\frac{1}{e}[W_q^p - W_{q''}^p] = \underset{(\text{inside the Lorentz sphere})}{\sum_{q'(\neq q)} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3}} - \underset{(\text{inside the Lorentz sphere})}{\sum_{q'(\neq q'')} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}''-\underset{\sim}{q}')}{|\underset{\sim}{q}''-\underset{\sim}{q}'|^3}}$$

$$+\underset{(\text{outside the Lorentz sphere})}{\sum_{q'} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3}} - \underset{(\text{outside the Lorentz sphere})}{\sum_{q'} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}''-\underset{\sim}{q}')}{|\underset{\sim}{q}''-\underset{\sim}{q}'|^3}} \equiv A' + B', \quad (2.4\text{-}31)$$

where A' is the first two summations and B' is the rest of the

right-hand side of (2.4-31).

Calculation of the summation A' : Because of the translational symmetry A' is reduced to the following sum, fig. (2.8):

$$A' = \sum_{\underset{\sim}{q}'} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} - \sum_{\underset{\sim}{q}'} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}''-\underset{\sim}{q}')}{|\underset{\sim}{q}''-\underset{\sim}{q}'|^3} \quad . \tag{2.4-32}$$

(on the hemispherical surface (b)) (on the semispherical surface (a))

Since we choose $R \gg a$, where a is the lattice distance, we can assume that $\underset{\sim}{q}$ and $\underset{\sim}{q}''$ are at the centre of the Lorentz sphere and we can make continuum approximation to calculate (2.4-32):

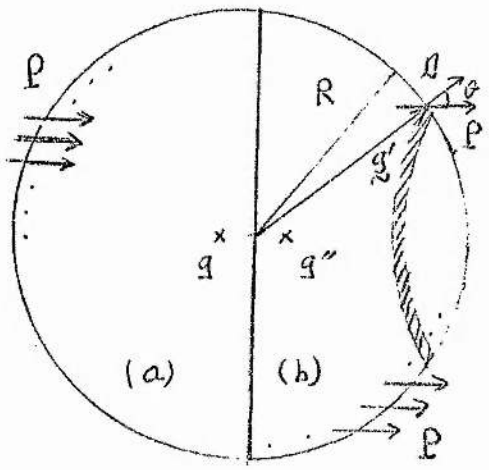


Figure (2.8)

$$A' = \underset{\text{(over the semi-spherical surface (b))}}{\int} \frac{d\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} - \underset{\text{(over the semi-spherical surface (a))}}{\int} \frac{d\underset{\sim}{p}\cdot(\underset{\sim}{q}''-\underset{\sim}{q}')}{|\underset{\sim}{q}''-\underset{\sim}{q}'|^3}$$

$$= -\int_0^{\frac{\pi}{2}} \frac{dp\, R\cos\theta}{R^3} - \int_0^{\frac{\pi}{2}} \frac{dp\, R\cos\theta}{R^3} = \frac{4\pi}{3} p a \quad . \tag{2.4-33}$$

Calculation of the summation B' :

$$B' = \sum_{\underset{\sim}{q}'} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^2} - \sum_{\underset{\sim}{q}'} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}''-\underset{\sim}{q}')}{|\underset{\sim}{q}''-\underset{\sim}{q}'|^2} \quad . \tag{2.4-34}$$

(outside the Lorentz sphere) (outside the Lorentz sphere)

Let $\underset{\sim}{q}'' = \underset{\sim}{q} + \underset{\sim}{h}$ in (2.4-34), where $\underset{\sim}{h}$ is the vector going from the point $\underset{\sim}{q}$ to $\underset{\sim}{q}''$ and $|\underset{\sim}{h}| = a$. So (2.4-34) becomes

$$B' = \sum_{\substack{\underset{\sim}{q}' \\ \text{(outside the Lorentz sphere)}}} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} - \sum_{\substack{\underset{\sim}{q}' \\ \text{(outside the Lorentz sphere)}}} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}'+\underset{\sim}{h})}{|\underset{\sim}{q}-\underset{\sim}{q}'+\underset{\sim}{h}|^3} . \qquad (2.4\text{-}35)$$

Since for the volume outside the Lorentz sphere the condition $|\underset{\sim}{q}-\underset{\sim}{q}'| \gg |\underset{\sim}{h}|$ holds, we can expand the second term in (2.4-35) in a Taylor series:

$$\sum_{\substack{\underset{\sim}{q}' \\ \text{(outside the Lorentz sphere)}}} \frac{\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}'+\underset{\sim}{h})}{|\underset{\sim}{q}-\underset{\sim}{q}'+\underset{\sim}{h}|^3} = \sum_{\underset{\sim}{q}'} \underset{\sim}{p}\cdot\left[\frac{(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} + \frac{\underset{\sim}{h}}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} - \frac{(\underset{\sim}{q}-\underset{\sim}{q}')\,3\,\underset{\sim}{h}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^5} - \mathcal{O}(h^2)\right] \qquad (2.4\text{-}36)$$

Substitution of (2.4-36) into (2.4-35) gives

$$B' = \sum_{\substack{\underset{\sim}{q}' \\ \text{(outside the Lorentz sphere)}}} \underset{\sim}{h}\cdot\left[\frac{\{3\,\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')\}(\underset{\sim}{q}-\underset{\sim}{q}') - |\underset{\sim}{q}-\underset{\sim}{q}'|^2\underset{\sim}{p}}{|\underset{\sim}{q}-\underset{\sim}{q}'|^5}\right] \qquad (2.4\text{-}37)$$

or

$$B' = \underset{\sim}{h}\cdot\left[\sum_{\substack{\underset{\sim}{q}' \\ \text{(outside the Lorentz sphere)}}} \frac{\{3\,\underset{\sim}{p}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')\}(\underset{\sim}{q}-\underset{\sim}{q}') - |\underset{\sim}{q}-\underset{\sim}{q}'|^2\underset{\sim}{p}}{|\underset{\sim}{q}-\underset{\sim}{q}'|^5}\right] . \qquad (2.4\text{-}38)$$

It is easily seen that the square bracket in (2.4-38) is the dipole field contribution to the point $\underset{\sim}{q}$ from all the dipoles outside the Lorentz sphere. So this field must be equal to depolarization field, $\underset{\sim}{E}_1$, plus the Lorentz field, $\underset{\sim}{E}_2$. So (2.4-38) becomes

$$B' = \underset{\sim}{h} \cdot (\underset{\sim}{E}_1 + \underset{\sim}{E}_2) \quad . \tag{2.4-39}$$

Substitution of (2.4-33) and (2.4-39) into (2.4-31) gives

$$-\frac{1}{e}\left[W_q^{\rho} - W_{q''}^{\rho}\right] = -\frac{4\pi}{3}\rho a + \underset{\sim}{h} \cdot (\underset{\sim}{E}_1 + \underset{\sim}{E}_2) \quad . \tag{2.4-40}$$

Substitution of the value of $\underset{\sim}{E}_2 = \frac{4\pi}{3}\underset{\sim}{\rho}$ into (2.4-40) $\left[W_q^{\rho} - W_{q''}^{\rho}\right]$ becomes

$$W_q^{\rho} - W_{q''}^{\rho} = -e\,\underset{\sim}{h} \cdot \underset{\sim}{E}_1 = e\,\underset{\sim}{E}_1 \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') \quad . \tag{2.4-41}$$

The results found in (2.4-29) and (2.4-41) can easily be generalized to any sample in the shape of a general ellipsoid of revolution, namely

$$W_q^{\rho} - W_{q''}^{\rho} = e\,\underset{\sim}{E}_1 \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') \tag{2.4-42}$$

with $\underset{\sim}{E}_1 = -N\underset{\sim}{P}$, depolarization field, where N is the appropriate depolarization factor. For justification of (2.4-42) the reader is referred to Appendix 2G where we calculate W_q^{ρ} itself for samples in the shape of a slab and a sphere and prove the

following theorem, namely: For a sample in the shape of a general ellipsoid of revolution W_q^p has the form

$$W_q^p = e E_1 \cdot (\underset{\sim}{q} - \underset{\sim}{q}_0) \quad , \tag{2.4-43}$$

where $\underset{\sim}{q}_0$ is the vector going to the centre of mass.

From (2.4-42) and (2.4-1), the net electric field appearing in the jump rate, and hence in the hopping conductivity is given by

$$e \underset{\sim}{E}_0 \cdot (\underset{\sim}{q} - \underset{\sim}{q}') + [W_q^p - W_{q'}^p] = e (\underset{\sim}{E}_0 + \underset{\sim}{E}_1) \cdot (\underset{\sim}{q} - \underset{\sim}{q}') = e \underset{\sim}{E}_{mac} \cdot (\underset{\sim}{q} - \underset{\sim}{q}') \tag{2.4-44}$$

and is simply equal to E_{mac}, the macroscopic electric field, due to all charges external and internal to the specimen. Under constant voltage conditions, this is identical to the field which would exist in the absence of the dielectric.

We note that although the above result was obtained for Bravais lattices with equal dipoles at each site, it can easily be generalized to a lattice with a basis as well provided that hopping occurs on the same sublattice. The reason for this is that the quantity $(W_q^p - W_{q'}^p)$ depends on the difference in energy at the two sites involved in the site jump. Because of this the short-range and Lorentz contributions to the dipolar potentials at the two sites cancel in detail, and one is left only with the contribution of dipoles on the outer surface of the specimen. This contribution, when added to that due to external charges, gives just the macroscopic electric field unmodified by the local field corrections.

The examples of the perfect crystalline materials to which our result can be applied are the alkali halides[34] and orthorhombic sulphur[35]. However there exist some crystalline materials like ferrites and garnets[18] in which the small polaron hopping may take

place between different sublattices as well, i.e., from octahedral to tetrahedral sites and from tetrahedral to octahedral sites. So in taking the difference, $[W_{\underline{q}}^{\rho} - W_{\underline{q}''}^{\rho}]$, the short range contributions do not cancel completely and $[W_{\underline{q}}^{\rho} - W_{\underline{q}'}^{\rho'}]$ can be written approximately as

$$W_{\underline{q}}^{\rho} - W_{\underline{q}''}^{\rho} = e\,\underset{\sim}{E}_1 \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') + e\,\underset{\sim}{E}_h \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') \,, \tag{2.4-45}$$

where $\underset{\sim}{E}_h = \underset{\sim}{E}_3^{\underline{q}} - \underset{\sim}{E}_3^{\underline{q}''}$. And $\underset{\sim}{E}_3^{\underline{q}}$ and $\underset{\sim}{E}_3^{\underline{q}''}$ are the E_3 fields at lattice sites $\underset{\sim}{q}$ and $\underset{\sim}{q}''$ respectively. In this case the net electric field appearing in the jump rate is given by

$$e\,\underset{\sim}{E}_0 \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') + [W_{\underline{q}}^{\rho} - W_{\underline{q}''}^{\rho}] = e(\underset{\sim}{E}_0 + \underset{\sim}{E}_1) \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') + e\,\underset{\sim}{E}_h \cdot (\underset{\sim}{q} - \underset{\sim}{q}'')$$

$$= e\,(\underset{\sim}{E}_{mac} + \underset{\sim}{E}_h) \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') \tag{2.4-46}$$

and is equal to $\underset{\sim}{E}_{mac} + \underset{\sim}{E}_h$.

In the following section we extend the present theory to the case of hopping between different sublattices.

Extension of the present theory to hopping between different sublattices:

2.5a Introduction:

This is the situation that may occur in ferrites and garnets in which two types of centres A and B are present separated by an energy ΔU (figure 2.11). We assume that $\Delta U \gg kT$ and that conduction is due to hopping between A sites but in each case the carrier must hop over an intermediate B site.

The ferrites are derived from crystalline Fe_2O_4 by substituting divalent and trivalent metal ions for irons while garnets are derived from crystalline ytrium oxide by substituting Fe^{2+} and Fe^{3+} for ytrium ions. Structurally both materials form cubic oxygen lattice with metal ions in octahedral and tetrahedral sites. Usually the Fe^{2+} ions show a preference for octahedral sites while Fe^{3+} ions can be found in both octahedral and tetrahedral sites in the ratio 1:1 for ferrites and 2:3 for garnets. The electron transport is ascribed to Fe^{2+} - Fe^{3+} exchange between sites. Normally the distribution of cation on the octahedral sites is random hence the distance between octahedral sites can be large and the electron may move indirectly via a tetrahedral site. The random distribution of cation on the octahedral sites leads to an energy spread W_D which is assumed to be very much smaller than kT .

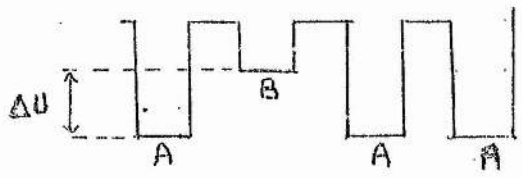


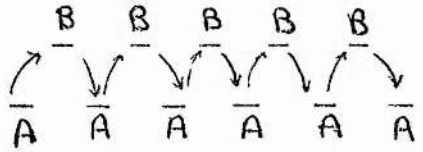
Figure (2.11)

If we denote octahedral sites by A and tetrahedral sites by B, since A and B sites are distributed randomly, the electron will move sometimes from A to A and sometimes from A to B, depending on the jump rate.

Now assuming that electrons always hop indirectly via a tetrahedral site, we can estimate the maximum enhancement in the macroscopic conductivity due to local field effect. In the following section this enhancement is derived on the basis of a model developed by Austin and Sayer[1].

2.5b: Calculation of the maximum enhancement in the conductivity for hopping between different sublattices in one dimension:

We assume hopping between two different sublattices A and B as illustrated in the figure, i.e. $A \to B \to A \to B \to A$.. and so on:



We denote the impedance of the hop from A to B by Z°_{ab}, and the impedance of the hop from B to A by Z°_{ba}.

In the absence of the applied field E_o, the average impedance per hop is

$$Z^{\circ}_{av} = \frac{n Z^{\circ}_{ab} + n Z^{\circ}_{ba}}{2n} = \frac{Z^{\circ}_{ab} + Z^{\circ}_{ba}}{2} , \qquad (2.5\text{-}1)$$

where $2n$ is the average number of links in the chain we consider (a number n of $A \to B$ type links and an equal number of $B \to A$ type links).

In the presence of an applied field E_o both Z°_{ab} and Z°_{ba} become reduced by a factor $\phi^{-1}(F_{ab})$ and $\phi^{-1}(F_{ba})$ respectively;

$$Z_{ab} = Z^{\circ}_{ab}\, \phi^{-1}(F_{ab}) , \qquad (2.5\text{-}2)$$

$$Z_{ba} = Z^{\circ}_{ba}\, \phi^{-1}(F_{ba}) , \qquad (2.5\text{-}3)$$

where $\phi(F_{ab})$ and $\phi(F_{ba})$ are given by the following expression; (in accordance with (2.3-53) and (2.4-46))

$$\phi(F_{ab}) = \frac{\sinh F_{ab}}{F_{ab}} , \quad F_{ab} = \frac{\beta e a}{2} E_{mac} + \frac{\beta e a}{2} E_h = F + \Delta , \qquad (2.5\text{-}4)$$

$$\phi(F_{ba}) = \frac{\sinh F_{ba}}{F_{ba}} , \quad F_{ba} = \frac{\beta e a}{2} E_{mac} - \frac{\beta e a E_h}{2} = F - \Delta , \qquad (2.5\text{-}5)$$

where $\beta = \frac{1}{kT}$, a is the average jump distance, E_{ab} is the local field across the hop $A \rightarrow B$ and E_{ba} is the one across the hop $B \rightarrow A$. Normally E_{ab} and E_{ba} can be written as; $E_{ab} = E_{mac} + E_h$ and $E_{ba} = E_{mac} - E_h$. Here E_h is the field due to hopping from A to B in the presence of induced dipoles: $E_h = E_3^A - E_3^B$, where E_3^A and E_3^B are the E_3 fields at lattice sites A and B respectively.

In the presence of an applied field E_o the average impedance per link becomes,

$$Z_{av} = \frac{n Z_{ab}^{\circ} \phi^{-1}(F_{ab}) + n Z_{ba}^{\circ} \phi^{-1}(F_{ba})}{2n} = \frac{Z_{ab}^{\circ} \phi^{-1}(F_{ab}) + Z_{ba}^{\circ} \phi^{-1}(F_{ba})}{2} \quad (2.5\text{-}6)$$

For average conduction we can write,

$$\frac{\langle \sigma(E) \rangle}{\langle \sigma(0) \rangle} = \frac{Z_{av}^{\circ}}{Z_{av}} = \frac{(Z_{ab}^{\circ} + Z_{ba}^{\circ})}{[Z_{ab}^{\circ} \phi^{-1}(F_{ab}) + Z_{ba}^{\circ}(F_{ba})]} \quad (2.5\text{-}7)$$

Next we write $\frac{F_{ab}}{F}$ and $\frac{F_{ba}}{F}$ in terms of impedances:

$$\frac{F_{ab}}{F} = \frac{F+\Delta}{F} = \frac{Z_{ab}^{\circ} \phi^{-1}(F_{ab})}{[Z_{ab}^{\circ} \phi^{-1}(F_{ab}) + Z_{ba}^{\circ} \phi^{-1}(F_{ba})]/2} \quad (2.5\text{-}8)$$

and

$$\frac{F_{ba}}{F} = \frac{F-\Delta}{F} = \frac{Z_{ba}^{\circ} \phi^{-1}(F_{ba})}{[Z_{ab}^{\circ} \phi^{-1}(F_{ab}) + Z_{ba}^{\circ} \phi^{-1}(F_{ba})]/2} \quad (2.5\text{-}9)$$

From (2.5-8) and (2.5-9) we can write

$$Z_{ab}^{\circ} = \frac{1}{2}\left(\frac{F+\Delta}{F}\right) \phi(F_{ab}) [Z_{ab}^{\circ} \phi^{-1}(F_{ab}) + Z_{ba}^{\circ} \phi^{-1}(F_{ba})] \quad (2.5\text{-}10)$$

and

$$Z^{\circ}_{ba} = \frac{1}{2}\left(\frac{F-\Delta}{F}\right)\phi(F_{ba})\left[Z^{\circ}_{ab}\,\phi^{-1}(F_{ab}) + Z^{\circ}_{ba}\,\phi^{-1}(F_{ba})\right] . \tag{2.5-11}$$

Substitution of (2.5-10) and (2.5-11) in the numerator of (2.5-7) gives

$$\frac{\langle\sigma(E)\rangle}{\langle\sigma(0)\rangle} = \frac{1}{2}\left[\phi(F_{ab}) + \phi(F_{ba})\right] + \frac{1}{2}\frac{\Delta}{F}\left[\phi(F_{ab}) - \phi(F_{ba})\right] . \tag{2.5-12}$$

Substituting the value of $\phi(F_{ab})$ and $\phi(F_{ba})$ from (2.5-4) and (2.5-5) into (2.5-12) we get

$$\frac{\langle\sigma(E)\rangle}{\langle\sigma(0)\rangle} = \frac{\sinh F}{F}\cosh\Delta = \frac{\sinh[\beta e a E_{mac}/2]}{\beta e a E_{mac}/2}\cosh\frac{\beta e a}{2}\left(E_3^{A} - E_3^{B}\right) . \tag{2.5-13}$$

From (2.5-13) it is seen that the macroscopic conductivity becomes modified by the factor of $\cosh\left[\frac{\beta e a}{2}\left(E_3^{A} - E_3^{B}\right)\right]$.

Numerical analysis: Assuming that the total polarizability arises from the oxygen ions we can say that the E_3 field at an octahedral site is zero, i.e., $E_3^{A} = 0$. On the other hand the field at a tetrahedral site is non-zero[25,28]. Let us assume that it is comparable with the Lorentz field $E_3^{B} \simeq E_2 = \frac{4\pi}{3}P$. On the basis of this assumption we can approximate (2.5-13) as follows:

$$\frac{\langle\sigma(E)\rangle}{\langle\sigma(0)\rangle} = \frac{\sinh\left[\beta e a E_{mac}/2\right]}{\left[\beta e a E_{mac}/2\right]}\cosh\left(\frac{\beta e a}{2}\,\frac{4\pi P}{3}\right) . \tag{2.5-14}$$

Using the well-known relation

$$\underset{\sim}{E}_{loc} = \underset{\sim}{E}_{mac} + \frac{4\pi}{3}\underset{\sim}{P} = \frac{2+\varepsilon}{3}\underset{\sim}{E}_{mac} \tag{2.5-15}$$

with ε as the static dielectric constant, we can substitute $\frac{4\pi}{3} P = \frac{\varepsilon-1}{3} E_{mac}$ in (2.5-14), hence

$$\frac{\langle\sigma(E)\rangle}{\langle\sigma(0)\rangle} = \frac{\sinh[\beta e a E_{mac}/2]}{[\beta e a E_{mac}/2]} \cosh\left[\frac{\beta e a}{2}\left(\frac{\varepsilon-1}{3}\right) E_{mac}\right]. \qquad (2.5\text{-}16)$$

Figure (2.12) shows $\langle\sigma(E)\rangle/\langle\sigma(0)\rangle$ versus E_{mac}/T for various values of ε. As is seen the enhancement is very small for low fields but can be very large for non-ohmic regions.

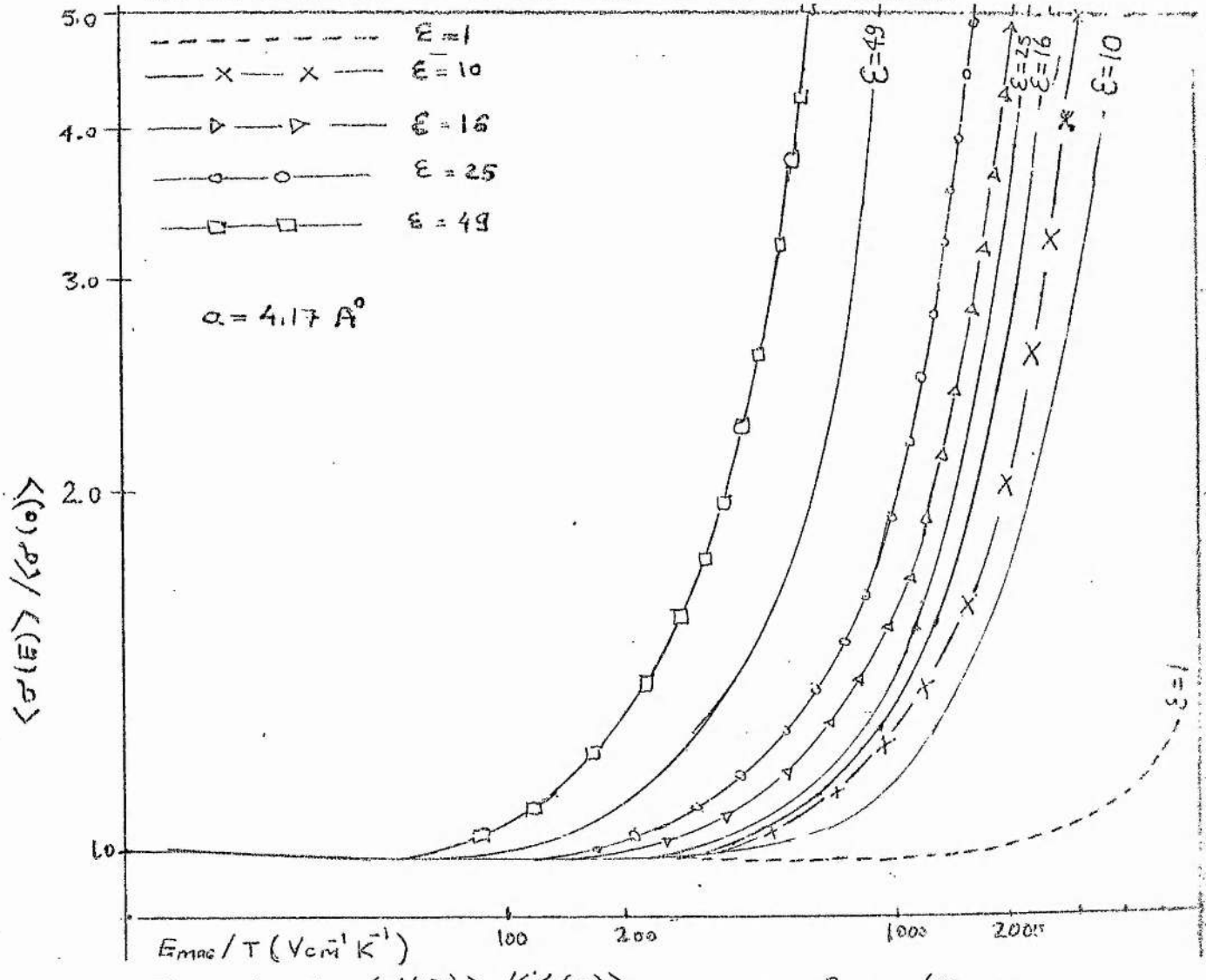


Figure (2.12): $\langle\sigma(E)\rangle/\langle\sigma(0)\rangle$ versus E_{mac}/T for various values of ε. The full lines correspond to $\sinh\left(\frac{\varepsilon+2}{3}\right)mx \Big/ \left(\frac{\varepsilon+2}{3}\right)mx$ plots.

2.6 Application of the present theory to the transition metal oxide glasses:

As was pointed out earlier, the present theory is a suitable generalization of the small polaron theory of Holstein which is based on the assumption of a regular periodic lattice. Therefore to apply the present theory to transition metal oxide glasses, it should be modified such as to describe their properties.

Schmid[2] has discussed the formation of the small polaron in transition metal oxide glasses, and given a more reasonable model of the glass lattice to which the small polaron theory was applied. The glass picture of Schmid is as follows: The glass structure consists of a random cation lattice embedded in the lattice of glass formers and anions. For example, in the case of the vanadium pentoxide glasses the vanadium ions form the random cation lattice and the phosphorous ions are the glass formers while the oxygen ions are the anions. The conduction electrons will be the 3d electrons of the transition metal cations which are strongly localized. It is also assumed that short range order is approximately preserved, namely, that the environment of each metal cation is random distortion of that appropriate to the stoichiometric transition metal oxide crystal.

Before giving the application of the present theory to the glass case it is expedient to consider the wave functions of the transition metal cations briefly. In the case of octahedral arrangements of oxygen ions, the 3d states of a transition metal cation split into six states of t_{2g} symmetry with orbital wave functions of the form

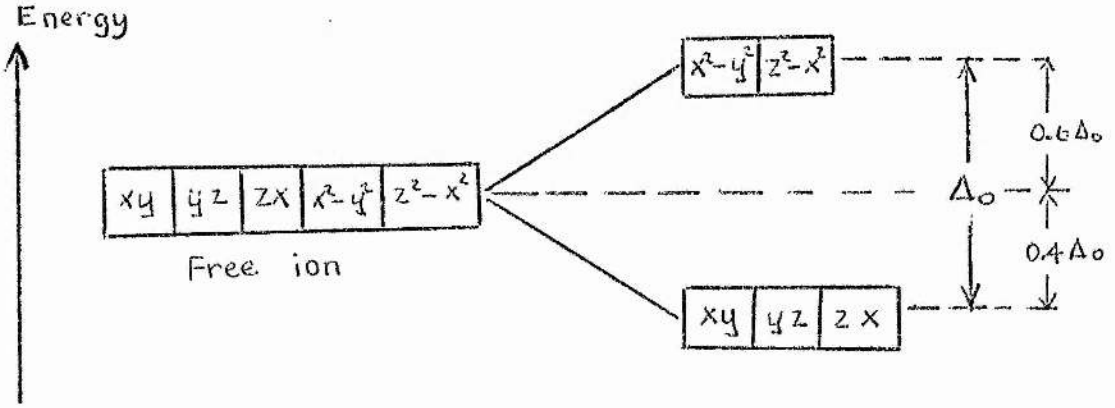
$$xy\, f(r)\,,\quad yz\, f(r)\,,\quad zx\, f(r)$$

and four states with e_g symmetry with wave functions

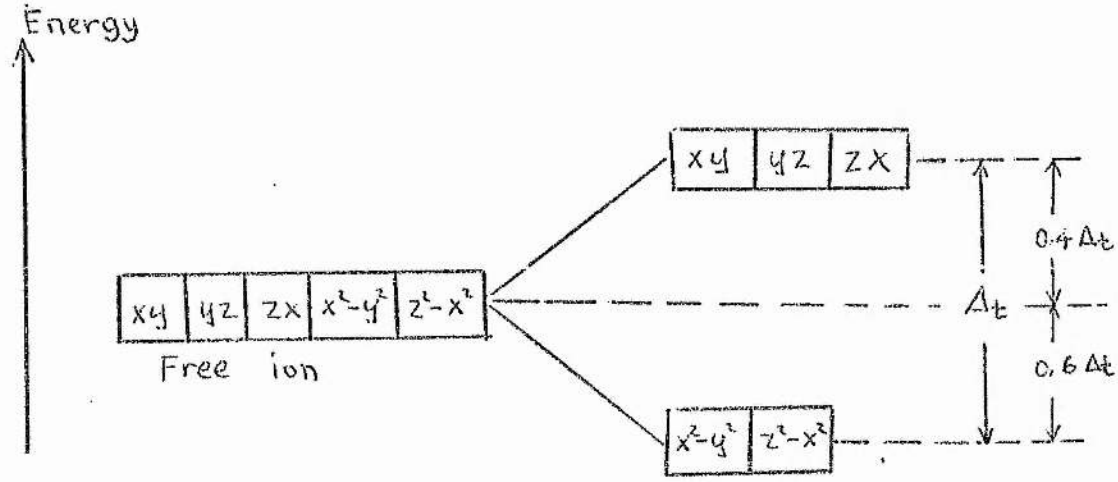
$$(x^2-y^2)f(r) \quad , \quad (z^2-x^2)\,f(r) \,.$$

The energy difference Δ_o between these states is called the "crystal field splitting", fig. (2.13a). On the other hand, in the case of tetrahedral arrangements of oxygen ions, the 3d states split in the reverse of octahedral arrangement, fig. (2.13b).

When transition metal oxides mix with P_2O_5 to form the glasses, we believe that because of the random distortions from the



(a)



(b)

Figure (2.13): Energy scheme for 3d orbitals

a) in octahedral arrangement, b) in tetrahedral arrangement.

stoichiometric transition metal oxide, the degeneracy of the above orbitals are removed and the electron occupies the ground states. Let us denote these orbitals $\phi_d^o(r)$ and $\phi_d^t(r)$ corresponding to octahedral and tetrahedral arrangements respectively.

To generalize our theory to the glass model, first we replace the previous local wave functions satisfying the equation (2.3-2) with the above $\phi_d^o(r)$ or $\phi_d^t(r)$ depending on octahedral or tetrahedral arrangements. The effect of the applied electric field to the present waves will be exactly the same as before, since they are real and have even parity. Hence for the glass case all the previous equations will be replaced with the present wave functions. The only difference is that the summations over the periodic lattices will be replaced by the summations over the random lattices. As long as the local field correction problem is concerned the summation (2.3-18) over the periodic lattice must be replaced by the three different summations over the random lattices, assuming $\underset{\sim}{q}$ is an octahedral site we can write

$$W_{\underset{\sim}{q}}^{\rho} = \int |\phi_d^o(\underset{\sim}{r}-\underset{\sim}{q})|^2 \sum_{\underset{\sim}{q}'\neq\underset{\sim}{q}} \frac{-e\rho_M\cdot(\underset{\sim}{r}-\underset{\sim}{q}')}{|\underset{\sim}{r}-\underset{\sim}{q}'|^3} + \int |\phi_d^o(\underset{\sim}{r}-\underset{\sim}{q})|^2 \sum_{\underset{\sim}{q}'} \frac{-e\rho_P\cdot(\underset{\sim}{r}-\underset{\sim}{q}')}{|\underset{\sim}{r}-\underset{\sim}{q}'|^3}$$

[over the random metal cations] [over the random glass formers]

(2.6-1)

$$+ \int |\phi_d^o(r-q)|^2 \sum_{\underset{\sim}{q}'} \frac{-e\rho_O\cdot(\underset{\sim}{r}-\underset{\sim}{q}')}{|\underset{\sim}{r}-\underset{\sim}{q}'|^3},$$

[over the random anions]

As was discussed in section (2.4) we can replace $|\phi_d^o(\underset{\sim}{r}-\underset{\sim}{q})|^2$ by delta functions at the lattice point $\underset{\sim}{q}$, so that from (2.6-1) we obtain

$$W_{\underset{\sim}{q}}^{\rho} = \sum_{\underset{\sim}{q}'\neq\underset{\sim}{q}} \frac{-e\rho_M\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} + \sum_{\underset{\sim}{q}'} \frac{-e\rho_P\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} + \sum_{\underset{\sim}{q}'} \frac{-e\rho_O\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3},$$

[over the random metal cations] [over the random glass formers] [over the random anions]

(2.6-2)

where P_m , P_p , P_o are the induced dipole moments of metal ions, phosphorous ions and oxygen ions respectively.

Further assuming that classical occurrence probability approach holds for random lattices we can generalize (2.3-43) to the random lattices, namely;

$$\omega_T(\underset{\sim}{q}\to\underset{\sim}{q}'') = \omega_T^{\circ}(\underset{\sim}{q}\to\underset{\sim}{q}'') \exp\left[e\,\underset{\sim}{E}_0\cdot(\underset{\sim}{q}-\underset{\sim}{q}'') + (W_q^p - W_{q''}^p)\right]/2kT \,, \tag{2.6-3}$$

where W_q^p and $W_{q''}^p$ are given according to (2.6-2).

To calculate W_q^p and $W_{q''}^p$ from (2.6-2) we assume that the total polarizability arises from the oxygen ions and the contribution of the transition metal ions and glass formers to the polarizability is zero (i.e. $P_m = P_p = 0$). We then make use of the short-range order which extends to a few lattice spacings, namely: we construct the fictitious Lorentz spheres concentric with the points $\underset{\sim}{q}$ and $\underset{\sim}{q}''$. And we choose the radius of the Lorentz sphere about few lattice spacings and assume that the dipoles outside the Lorentz sphere can be approximated by a continuum. Then W_q^p can be written as

$$W_q^p = \underbrace{\sum_{\underset{\sim}{q}'} \frac{-e\,\underset{\sim}{P}_o\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3}}_{\left[\text{inside the Lorentz sphere}\right]} + \underbrace{\sum_{\underset{\sim}{q}'} \frac{-e\,\underset{\sim}{P}_o\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3}}_{\left[\text{over the random anions outside the Lorentz sphere}\right]} \,. \tag{2.6-4}$$

Let us denote the short-range contribution to W_q^p by α_q . Since the random dipoles outside the Lorentz sphere can be approximated by a continuum, their contribution to the point $\underset{\sim}{q}$, in accordance with Appendix 2G, will be $e\,\underset{\sim}{E}_1\cdot(\underset{\sim}{q}-\underset{\sim}{q}_0)$. Hence (2.6-4) can be written as

$$W_q^p = \alpha_q + e\,\underset{\sim}{E}_1\cdot(\underset{\sim}{q}-\underset{\sim}{q}_0) \,. \tag{2.6-5}$$

Similarly $W_{g''}^{f}$ can be written as

$$W_{g''}^{f} = \alpha_{g''} + e\underset{\sim}{E}_{l}\cdot(\underset{\sim}{g}''-\underset{\sim}{g}_{0}) \quad . \tag{2.6-6}$$

Now if the sites $\underset{\sim}{g}$ and $\underset{\sim}{g}''$ are identical (both have octahedral or tetrahedral environments) the short-range contributions will be equal,

$$\alpha_{g} = \alpha_{g''} \quad . \tag{2.6-7}$$

So in taking the difference $[W_{g}^{f} - W_{g''}^{f}]$ the short-range contributions cancel and we can write,

$$W_{g}^{f} - W_{g''}^{f} = e\,\underset{\sim}{E}_{l}\cdot(\underset{\sim}{g}-\underset{\sim}{g}'') \quad . \tag{2.6-8}$$

Substitution of (2.6-8) into (2.6-3) gives

$$\omega_{T}(\underset{\sim}{g}\rightarrow\underset{\sim}{g}'') = \omega_{T}^{\circ}\,(g-g'')\,exp\left[e\,E_{macl}\,(g-g'')\right] \quad , \tag{2.6-9}$$

i.e. no local field correction to the jump rate.

On the other hand, if the sites $\underset{\sim}{g}$ and $\underset{\sim}{g}''$ are not identical, for example $\underset{\sim}{g}$ has an octahedral arrangement and $\underset{\sim}{g}''$ has a tetrahedral arrangement of oxygen ions, the short-range contributions will not be equal, $\alpha_{g} \neq \alpha_{g''}$. This will lead to local field type corrections to jump rate, and hence to the hopping conductivity.

In transition metal oxide glasses, because of the mixed valency, we believe that metal ions can be found in both octahedral and tetrahedral sites (like ferrites and garnets). Hence in taking the difference $[W_{g}^{f} - W_{g''}^{f}]$, short-range contributions do not cancel in detail and $[W_{g}^{f} - W_{g''}^{f}]$ can be written approximately, in accordance with (2.4-45), as

$$W_{g}^{f} - W_{g''}^{f} = e\,\underset{\sim}{E}_{l}\cdot(\underset{\sim}{g}-\underset{\sim}{g}'') + e\,\underset{\sim}{E}_{h}\cdot(\underset{\sim}{g}-\underset{\sim}{g}'') \quad , \tag{2.6-10}$$

where $\underset{\sim}{E}_h = \underset{\sim}{E}_3^{q} - \underset{\sim}{E}_3^{q''}$ is the difference of the E_3 fields at sites $\underset{\sim}{q}$ and $\underset{\sim}{q}''$.

In line with section (2.5-b) the above extra term $e\,\underset{\sim}{E}_h \cdot (\underset{\sim}{q} - \underset{\sim}{q}'')$ will give rise to a considerable enhancement in the macroscopic conductivity. As was seen from figure (2.12) at higher fields the resulting effective field can be as high as $\underset{\sim}{E}_{loc}$ which might account for the large experimental jump parameters.

2.7 Conclusions:

We have investigated the local field corrections to a particular kind of hopping mechanism, namely the small polaron hopping conduction. This has been shown by a natural extension of the existing theory of Holstein.

The result of this chapter can be summarized as follows:

For crystalline case, local field corrections are absent if hopping occurs on the same sublattice. However, for hopping between different sublattices, local field corrections can exist and, while negligible at low fields $(eaE_{max} < kT)$, can be considerable for high fields.

For glasses, as a result of short range order, similar results have been obtained. Namely, no local field corrections for hopping between identical sites but possible local field corrections for hopping between non-identical sites especially at high fields.

(APPENDIX 2A)

Comparison of $\left[J^{\rho}(X_q, X_{qrh}) - S_{g,qrh} W^{\rho}_{qrh} \right]$ with $J(X_q, X_{qrh})$:

Recall (2.3-9), (2.3-16) and (2.3-18). Noting that the basic functions are real and by setting X_g equal to zero in accordance with the assumption (b) in the text we can write,

$$S_{g,qrh} = \int \phi(\underset{\sim}{r}-\underset{\sim}{g})\ \phi(\underset{\sim}{r}-\underset{\sim}{g}-\underset{\sim}{h})\, dV \quad , \tag{2A.1}$$

$$J^{\rho}(X_q, X_{qrh}) = \int \phi(\underset{\sim}{r}-\underset{\sim}{g}) \sum_{\underset{\sim}{g}''\neq \underset{\sim}{g}+\underset{\sim}{h}} \frac{-e\,\underset{\sim}{\rho}\cdot(\underset{\sim}{r}-\underset{\sim}{g}'')}{|\underset{\sim}{r}-\underset{\sim}{g}''|^3}\ \phi(\underset{\sim}{r}-\underset{\sim}{g}-\underset{\sim}{h})\, dV \tag{2A.2}$$

and

$$W^{\rho}_{qrh} = \int |\phi(\underset{\sim}{r}-\underset{\sim}{g}-\underset{\sim}{h})|^2 \sum_{g''\neq g+h} \frac{-e\,\underset{\sim}{\rho}\cdot(\underset{\sim}{r}-\underset{\sim}{g}'')}{|\underset{\sim}{r}-\underset{\sim}{g}''|^3}\, dV \, . \tag{2A.3}$$

Transforming the integration variable to $\underset{\sim}{\rho} = \underset{\sim}{r} - \underset{\sim}{g} - \underset{\sim}{h}$ and expanding the summation about $\rho = 0$, (2A.2) becomes

$$J^{\rho}(X_q, X_{qrh}) = \int \phi(\rho+h) \left[\sum_{g''\neq g+h} \frac{-e\,\underset{\sim}{\rho}\cdot(\underset{\sim}{g}+\underset{\sim}{h}-\underset{\sim}{g}'')}{|g+h-g''|^3} + \left(\frac{\partial V}{\partial r}\right)_{\underset{\sim}{\rho}=0} \underset{\sim}{\rho} + \cdots \right] \phi(\rho)\, dV \tag{2A.4}$$

where V stands for the summation in (2A.2). It is noted that the coefficient of $\underset{\sim}{\rho}$ in the square bracket is simply equal to $e(\underset{\sim}{E}_1 + \underset{\sim}{E}_2)$ where $\underset{\sim}{E}_1$ is the depolarization field and $\underset{\sim}{E}_2$

is the Lorentz field and both are proportional to the applied field,

$$\left(\frac{\partial V}{\partial r}\right)_{\rho=0} = \left(\frac{\partial V}{\partial r}\right)_{r=q+h} = e\,(E_1 + E_2) = e\,\alpha\,E_0 \quad , \text{ with } \quad |\alpha| < 1 \quad .$$

(2A.5)

With the above definition (2A.4) can be written as

$$J^{\rho}(x_q, x_{q+h}) = \sum_{q' \neq q+h} \frac{-e\,\rho\cdot(q+h-q')}{|q+h-q'|^3} \int \phi(\rho+h)\,\phi(\rho)\,dV + \alpha E_0 \cdot \int \phi(\rho)\,\rho\,\phi(\rho+h)\,dV \quad .$$

(2A.6)

Further, equation (2A.3) can be simplified by noting that the question at hand applies equally to the case of point charges and nothing of principle is gained by averaging the dipolar potentials over a finite wave function. Hence the latter are taken to be delta functions at the lattice sites so that from (2A.3) we can write

$$W^{\rho}_{q+h} = \sum_{q' \neq q+h} \frac{-e\,\rho\cdot(q+h-q')}{|q+h-q'|^3} \quad . \qquad (2A.7)$$

Comparing (2A.6) with (2A.1) and (2A.7) we can write

$$J^{\rho}(x_q, x_{q+h}) = W^{\rho}_{q+h}\,\delta_{q,q+h} + e\,\alpha\,E_0 \cdot \int \phi(\rho+h)\,\rho\,\phi(\rho)\,dV \qquad (2A.8)$$

or

$$J^{\rho}(x_q, x_{q+h}) - \delta_{q,q+h}\,W^{\rho}_{q+h} = e\,\alpha\,E_0 \cdot \int \phi(\rho+h)\,\rho\,\phi(\rho)\,dV \quad . \qquad (2A.9)$$

Transforming the integration variable to $\rho = \rho - \frac{h}{2}$, (2A.9) becomes

$$J^{\rho}(x_g, x_{g+h}) - S_{g,g+h} W^{\rho}_{g+h} = -e\frac{\alpha}{2} E_0 \cdot h \int \phi(\underline{r}+\tfrac{h}{2})\,\phi(\underline{r}-\tfrac{h}{2})\,dV$$

$$= -e\frac{\alpha}{2} E_0 \cdot h\, S_{g,g+h} = e\frac{\alpha}{2} a E_0 S_{g,g+h} \,. \tag{2A.10}$$

On the other hand $J(x_g, x_{g+h})$ can be written as

$$J(x_g, x_{g+h}) \approx -W_{\rho} S_{g,g+h} \,, \tag{2A.11}$$

where W_{ρ} is the binding energy of the small polaron*.

Sample numerical calculation:

We use the numerical estimates of reference (20) and take typical values for the experimental conditions:

$$E_0 \approx 5 \times 10^{5} \; V\,cm^{-1}$$

$$a \approx 5 \times 10^{-8} \; cm$$

$$\alpha \approx 1$$

$$W_{\rho} \approx 0{,}5 \; eV$$

Then according to (2A.10) and (2A.11)

$$\frac{J^{\rho}(x_g, x_{g+h}) - S_{g,g+h} W_{g+h}}{J(x_g, x_{g+h})} \approx 5 \times 10^{-2} \,. \tag{2A.12}$$

Therefore at fields which we are interested in, the term $[J^{\rho}(x_g, x_{g+h}) - S_{g,g+h} W_{g+h}]$ becomes very much smaller than $J(x_g, x_{g+h})$, hence can be neglected.

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*For justification of this c.f. reference (26) where J is found to be $J = -\frac{e^2}{K_0 a} S$, with $\frac{e^2}{K_0 a}$ the binding energy.

(APPENDIX 2B)

Evaluation of the integral

$$S_g^{(b)} = -BP \int \sum_{\lambda'} \delta(\underset{\sim}{\sigma} - \underset{\sim}{\sigma}_{\lambda'}) \frac{1}{(\sigma^2 + \lambda_3^2 \alpha_3^2)^{3/2}} d^2\underset{\sim}{\sigma} \qquad (2B.1)$$

Now for a simple cubic lattice, we have $\alpha_3^2 = 1$ and $\sigma_{\lambda'}^2 = \lambda_1^2 + \lambda_2^2$. Therefore, (2B.1) becomes

$$S_g^{(b)} = -BP \sum_{\lambda'} \delta(\underset{\sim}{\sigma} - \underset{\sim}{\sigma}_{\lambda'}) \frac{1}{(\underset{\sim}{\sigma}^2 + \lambda_3^2)^{3/2}} d^2\underset{\sim}{\sigma} , \qquad (2B.2)$$

by two-dimensional Fourier transform (FT_2) , we can transform the two-dimensional sum into an equivalent sum over the corresponding two-dimensional reciprocal lattice (Parseval's theorem). So (2B.2) becomes

$$S_g^{(b)} = -BP \int FT_2 \left[\sum_{\lambda'} \delta(\underset{\sim}{\sigma} - \underset{\sim}{\sigma}_{\lambda'}) \right] FT_2 \left[\frac{1}{(\sigma^2 + \lambda_3^2)^{3/2}} \right] d^2\underset{\sim}{h} , \qquad (2B.3)$$

where $d^2\underset{\sim}{h}$ is the area in reciprocal space.

It will be shown in Appendix 2C that

$$FT_2 \left[\sum_{\lambda'} \delta(\underset{\sim}{\sigma} - \underset{\sim}{\sigma}_{\lambda'}) \right] = \sum_{\lambda'} \delta(\underset{\sim}{h} - \underset{\sim}{h}_{\lambda'}) , \qquad (2B.4)$$

where $\underset{\sim}{h}_{\lambda} = \lambda_1 \underset{\sim}{x}_1 + \lambda_2 \underset{\sim}{x}_2$ and $\underset{\sim}{x}_1 = \frac{\underset{\sim}{a}_1}{a}$; $\underset{\sim}{x}_2 = \frac{\underset{\sim}{a}_2}{a}$.

It will also be shown in Appendix 2E that

$$FT_2\left[\frac{1}{(\sigma^2+\lambda_3^2)^{3/2}}\right] = 4\pi h_x \int_{-\infty}^{\infty} dy \frac{e^{2\pi i y h_y} K_1\left[(y^2+\lambda_3^2)^{1/2} 2\pi h_x\right]}{(y^2+\lambda_3^2)^{1/2}}, \quad (2B.5)$$

where K_1 is the modified Bessel function of second kind.

Substitution of (2B.4) and (2B.5) into (2B.3) gives.

$$S_g^{(b)} = -BP \iint \left\{ \sum_{\lambda} \delta(\underset{\sim}{h} - \underset{\sim}{h}_{\lambda}) 4\pi h_x \int_{-\infty}^{\infty} dy \frac{e^{2\pi i y h_y} K_1\left[(y^2+\lambda_3^2)^{1/2} 2\pi h_x\right]}{(y^2+\lambda_3^2)^{1/2}} \right\} d^2h . \quad (2B.6)$$

By interchanging the summation and the integral we have

$$S_g^{(b)} = -BP \sum_{\lambda} \int \left[\iint \delta(\underset{\sim}{h} - \underset{\sim}{h}_{\lambda}) 4\pi h_x \int_{-\infty}^{\infty} dy \frac{e^{2\pi i y h_y} K_1\left[(y^2+\lambda_3^2)^{1/2} 2\pi h_x\right]}{(y^2+\lambda_3^2)^{1/2}} \right] d^2h \quad (2B.7)$$

or

$$S_g^{(b)} = -BP \sum_{\lambda} 4\pi h_{\lambda_1} \int_{-\infty}^{\infty} dy \frac{e^{2\pi i y h_{\lambda_2}} K_1\left[(y^2+\lambda_3^2)^{1/2} 2\pi h_{\lambda_1}\right]}{(y^2+\lambda_3^2)^{1/2}} . \quad (2B.8)$$

Replacing $h_{\lambda_1} = \lambda_1$ and $h_{\lambda_2} = \lambda_2$ where λ_1 and λ_2 are integers ($\lambda_1, \lambda_2 = 0, \pm 1, \pm 2, \ldots$) we have

$$S_g^{(b)} = -BP\sum_{\lambda'} 4\pi\lambda_1 \int_{-\infty}^{\infty} dy \frac{e^{2\pi i y\lambda_2} H_1\left[(y^2+\lambda_3^2)^{1/2} 2\pi\lambda_1\right]}{(y^2+\lambda_3^2)^{1/2}} \tag{2B.9}$$

or

$$S_g^{(b)} = -BP\,4\pi \int_{-\infty}^{\infty} \left\{ \sum_{\lambda_2} e^{2\pi i y\lambda_2} \sum_{\lambda_1} \frac{H_1\left[(y^2+\lambda_3^2)^{1/2} 2\pi\lambda_1\right]}{(y^2+\lambda_3^2)^{1/2}} \right\} dy \tag{2B.10}$$

Now substitute

$$\sum_{\lambda_2} e^{2\pi i y\lambda_2} = \sum_{n} \delta(y-n) \quad ; \quad \text{(2D.10) into (2B.10),}$$

where n are integers. We have

$$S_g^{(b)} = -4\pi BP \int_{-\infty}^{\infty} \left\{ \sum_{n} \delta(y-n) \sum_{\lambda_1} \lambda_1 \frac{H_1\left[(y^2+\lambda_3^2)^{1/2} 2\pi\lambda_1\right]}{(y^2+\lambda_3^2)^{1/2}} \right\} dy \tag{2B.11}$$

or

$$S_g^{(b)} = -4\pi BP \sum_{n,\lambda_1} \lambda_1 \frac{H_1\left[(n^2+\lambda_3^2)^{1/2} 2\pi\lambda_1\right]}{(n^2+\lambda_3^2)^{1/2}} \tag{2B.12}$$

Because of the properties of $K_1(z)$ function (Appendix 2F), the only non-zero contribution to the sum comes from the term $\lambda_1 = 0$. Using (2F.2), we can write

$$\lim_{\lambda_1 \to 0} \left\{ \lambda_1 K_1 \left[(n^2 + \lambda_3^2)^{1/2} 2\pi \lambda_1 \right] \right\} = \lim_{\lambda_1 \to 0} \lambda_1 \frac{1}{(n^2 + \lambda_3^2) 2\pi \lambda_1} = \frac{1}{2\pi (n^2 + \lambda_3^2)^{1/2}} . \tag{2B.13}$$

Substituting (2B.13) into (2B.12), we get

$$S_g^{(b)} = -2BP \sum_{n=-\infty}^{\infty} \frac{1}{(n^2 + \lambda_3^2)} \tag{2B.14}$$

which is equal to

$$S_g^{(b)} = -\frac{2\pi BP}{\lambda_3} \coth(\pi \lambda_3) . \tag{2B.15}$$

Here we put

$$\sum_{n=-\infty}^{\infty} \frac{1}{n^2 + \lambda_3^2} = \frac{\pi}{\lambda_3} \coth(\pi \lambda_3) \tag{2B.16}$$

(for the value of this sum see for instance reference 21, p.467).

APPENDIX 2C

Proof of the relation; $FT_2\left[\sum_{\lambda'} \delta(\underline{\sigma}-\underline{\sigma}_{\lambda'})\right]=\sum_{\lambda'} \delta(\underline{h}-\underline{h}_{\lambda'})$:

The three-dimensional Fourier transform of a function $f(\underline{r})$ is defined by

$$FT_3\left[f(\underline{r})\right]=\int f(\underline{r})\exp(2\pi i\,\underline{h}\cdot\underline{r})\,d^3r \equiv F(\underline{h}) \tag{2C.1}$$

The inversion is

$$FT_3\left[F(\underline{h})\right]=\int F(\underline{h})\exp(-2\pi i\,\underline{h}\cdot\underline{r})\,d^3h = f(\underline{r}) \,. \tag{2C.2}$$

A well-known formal expression for the δ -function is

$$\delta(\underline{r}-\underline{\xi}) = \int \exp\left[-2\pi i\,\underline{h}\cdot(\underline{r}-\underline{\xi})\right] d^3h \,, \tag{2C.3}$$

for which we can write

$$\delta(\underline{r}-\underline{\xi}) = FT_3\left[\exp(2\pi i\,\underline{h}\cdot\underline{\xi})\right] \,. \tag{2C.4}$$

By inversion

$$FT_3\left[\delta(\underline{r}-\underline{\xi})\right] = \exp(2\pi i\,\underline{h}\cdot\underline{\xi}) \,. \tag{2C.5}$$

In a similar way, we can derive the two-dimensional Fourier transform of the function $\sum_{\lambda'} \delta(\underline{\sigma}-\underline{\sigma}_{\lambda'})$ which has δ-singularities at the points $\underline{\sigma}_{\lambda'}$ and which is zero elsewhere. One finds;

$$FT_2\left[\sum_{\lambda'} \delta(\underline{\rho}-\underline{\rho}_{\lambda'})\right] \equiv \sum_{\lambda'} FT_2\left[\delta(\underline{\rho}-\underline{\rho}_{\lambda'})\right] = \sum_{\lambda'} \exp(2\pi i\, \underline{h}\cdot\underline{\rho}_{\lambda'}) \,. \tag{2C.6}$$

In Appendix 2D we shall show that

$$\sum_{\lambda'} \exp(2\pi i\, \underline{h}\cdot\underline{\rho}_{\lambda'}) = \sum_{\lambda'} \delta(\underline{h}-\underline{h}_{\lambda'}) \,. \tag{2C.7}$$

From (2C.6) and (2C.7) we see that

$$FT_2\left[\sum_{\lambda'} \delta(\underline{\rho}-\underline{\rho}_{\lambda'})\right] = \sum_{\lambda'} \delta(\underline{h}-\underline{h}_{\lambda'}) \,. \tag{2C.8}$$

APPENDIX 2D

Proof of the relation.

$$\sum_{\lambda'} \exp\left(2\pi i\, \underset{\sim}{h}\cdot \underset{\sim}{g}_{\lambda'}\right) = \sum_{\lambda'} \delta\left(\underset{\sim}{h} - \underset{\sim}{h}_{\lambda'}\right) \; ; \tag{2D.1}$$

We start out from Poisson's sum* formula:

$$\sum_{n=-\infty}^{\infty} f(x-n) = \sum_{\nu=-\infty}^{\infty} \exp(2\pi i \nu x) \int_{-\infty}^{\infty} f(\xi)\, \exp(-2\pi i \nu \xi)\, d\xi \; , \tag{2D.2}$$

Inserting for $f(x)$ the $\delta(x)$ function we find

$$\sum_{n=-\infty}^{\infty} \delta(x-n) = \sum_{\nu=-\infty}^{\infty} \exp(2\pi i \nu x) \; . \tag{2D.3}$$

Using $\underset{\sim}{g}_{\lambda'} = \sum_i \lambda_i \underset{\sim}{a}_i \; ; (i=1,2) \; ; \; \underset{\sim}{a}_i = \dfrac{\underset{\sim}{a}_i}{a}$, we can write for the left-hand side of (2D.1);

$$\sum_{\lambda'} \exp\left(2\pi i\, \underset{\sim}{h}\cdot \underset{\sim}{g}_{\lambda'}\right) = \sum_{\lambda'} \exp\left[2\pi i\, \underset{\sim}{h}\cdot \sum_i \lambda_i \underset{\sim}{a}_i\right] \equiv \sum_{\lambda'} \exp\left[2\pi i \sum_i \lambda_i \left(\underset{\sim}{h}\cdot \underset{\sim}{a}_i\right)\right]$$

$$\equiv \sum_{\lambda'} \left[\prod_i \exp\left(2\pi i\, \lambda_i \left(\underset{\sim}{h}\cdot \underset{\sim}{a}_i\right)\right)\right] \equiv \prod_i \sum_{\lambda_i} \exp\left[2\pi i\, \lambda_i \left(\underset{\sim}{h}\cdot \underset{\sim}{a}_i\right)\right] \; . \tag{2D.4}$$

By virtue of (2D.3), we can write (2D.4) as

$$\sum \exp\left(2\pi i\, \underset{\sim}{h}\cdot \underset{\sim}{g}_{\lambda'}\right) = \prod_i \sum_{\lambda_i} \delta\left(\underset{\sim}{h}\cdot \underset{\sim}{a}_i - \lambda_i\right) \equiv \sum_{\lambda'} \left[\prod_i \delta\left(\underset{\sim}{h}\cdot \underset{\sim}{a}_i - \lambda_i\right)\right]$$

or

*c.f. reference (27) p.28.

$$\sum_{\lambda'} \exp\left(2\pi i\, \underset{\sim}{h}\cdot \underset{\sim}{\sigma}_{\lambda'}\right) = \sum_{\substack{\lambda' \\ (\lambda_1,\lambda_2)}} \left[\prod_i \delta\left(\underset{\sim}{h}\cdot \underset{\sim}{\alpha}_i - \lambda_i\right)\right] . \tag{2D.5}$$

The integers λ_i $(i=1,2)$ may be written as $\lambda_i = \underset{\sim}{h}_{\lambda'}\cdot \underset{\sim}{\alpha}_i$.

Because; $\underset{\sim}{h}_{\lambda'} = \sum \lambda_J \underset{\sim}{\beta}_J$, $\underset{\sim}{\alpha}_i \cdot \underset{\sim}{h}_{\lambda'} = \sum_J \lambda_J \left(\underset{\sim}{\alpha}_i \cdot \underset{\sim}{\beta}_J\right) = \sum_J \lambda_J \delta_{iJ} = \lambda_i$

So (2D.5) becomes

$$\sum_{\lambda'} \exp\left(2\pi i\, \underset{\sim}{h}\cdot \underset{\sim}{\sigma}_{\lambda'}\right) = \sum_{\substack{\lambda' \\ (\lambda_1,\lambda_2)}} \left[\prod_i \delta\left(\underset{\sim}{h}\cdot \underset{\sim}{\alpha}_i - \underset{\sim}{h}_{\lambda'}\cdot \underset{\sim}{\alpha}_i\right)\right]$$

or

$$\sum_{\lambda'} \exp\left(2\pi i\, \underset{\sim}{h}\cdot \underset{\sim}{\sigma}_{\lambda'}\right) = \sum_{\substack{\lambda' \\ (\lambda_1,\lambda_2)}} \left\{\prod_i \delta\left[\left(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'}\right)\cdot \underset{\sim}{\alpha}_i\right]\right\} . \tag{2D.6}$$

Now choose another cartesian coordinate system $(\underset{\sim}{\gamma}_1, \underset{\sim}{\gamma}_2)$ from which $(\underset{\sim}{\alpha}_1, \underset{\sim}{\alpha}_2)$ can be obtained by a rotation transformation:

$$(\alpha) = \begin{pmatrix} \alpha_1 \\ \alpha_2 \end{pmatrix} = A \begin{pmatrix} \gamma_1 \\ \gamma_2 \end{pmatrix} = \begin{pmatrix} \alpha_{11} & \alpha_{12} \\ \alpha_{21} & \alpha_{22} \end{pmatrix} \begin{pmatrix} \gamma_1 \\ \gamma_2 \end{pmatrix} = A(\gamma) . \tag{2D.7}$$

So

$$\underset{\sim}{\alpha}_i = \sum_{J=1}^{2} \alpha_{iJ}\, \underset{\sim}{\gamma}_J = \left[A(\gamma)\right]_i , \tag{2D.8}$$

then

$$\left(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'}\right)\cdot \underset{\sim}{\alpha}_i = \left(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'}\right)\cdot\left[\sum_{J=1}^{2} \alpha_{iJ}\, \underset{\sim}{\gamma}_J\right] = \sum_{\ell=1}^{2} \left[\left(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'}\right)_\ell \underset{\sim}{\gamma}_\ell\right]\left[\sum_{J=1}^{2} \alpha_{iJ}\, \underset{\sim}{\gamma}_J\right]$$

$$= \sum_{\ell,J} \left(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'}\right)_\ell \alpha_{iJ}\left(\underset{\sim}{\gamma}_\ell \cdot \underset{\sim}{\gamma}_J\right) = \sum_J \left(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'}\right)_J \alpha_{iJ} ,$$

or

$$(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'})\cdot\underset{\sim}{\alpha}_i = \left[A\,(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'})\right]_i \quad . \tag{2D.9}$$

Substitution of (2D.9) into (2D.6) gives

$$\sum_{\lambda'} \exp(2\pi i\, \underset{\sim}{h}\cdot\underset{\sim}{\alpha}_{\lambda'}) = \sum_{\lambda'}\left\{\prod_i \delta\left[A\,(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'})_i\right]\right\} = \sum_{\lambda'} \delta\left[A(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'})\right]$$

or

$$\sum_{\lambda'} \exp(2\pi i\, \underset{\sim}{h}\cdot\underset{\sim}{\alpha}_{\lambda'}) = \frac{1}{|A|}\sum_{\lambda'} \delta(h-h_{\lambda'}) = \sum_{\lambda'} \delta(\underset{\sim}{h}-\underset{\sim}{h}_{\lambda'}) \,, \tag{2D.10}$$

since A is a rotation transformation, we put $|A| = 1$ in (2D.10).

APPENDIX 2E

Calculation of $FT_2\left[\frac{1}{(\sigma^2+\lambda_3^2)^{3/2}}\right]$:

From the definition;

$$FT_2\left[\frac{1}{(\underset{\sim}{\sigma}^2+\lambda_3^2)^{3/2}}\right] = \int \frac{e^{2\pi i(xh_x+yh_y)}}{(\underset{\sim}{\sigma}^2+\lambda_3^2)^{3/2}}\,dx\,dy \equiv \int \frac{e^{2\pi i(xh_x+yh_y)}}{(x^2+y^2+\lambda_3^2)^{3/2}}\,dx\,dy \quad . \tag{2E.1}$$

The double integral (2E.1) can be expressed as the iterated integral:

$$FT_2\left[\frac{1}{(\sigma^2+\lambda_3^2)^{3/2}}\right] = \int_{-\infty}^{\infty} e^{2\pi i y h_y}\left[\int_{-\infty}^{\infty} \frac{e^{2\pi i x h_x}}{(x^2+y^2+\lambda_3^2)^{3/2}}\,dx\right] dy \quad . \tag{2E.2}$$

or

$$FT_2\left[\frac{1}{(\sigma^2+\lambda_3^2)^{3/2}}\right] = \int dy\, e^{2\pi i y h_y} A \quad , \tag{2E.3}$$

where

$$A = \int_{-\infty}^{\infty} \frac{e^{2\pi i x h_x}}{(x^2+y^2+\lambda_3^2)^{3/2}}\,dx = \int_{-\infty}^{\infty} \frac{e^{2\pi i x h_x}}{(x^2+a^2)^{3/2}}\,dx \tag{2E.4}$$

with $a^2 = y^2+\lambda_3^2$.

Substituting $z = 2\pi h_x$ into (2E.4) we get

$$A = \int_{-\infty}^{\infty} \frac{e^{izx}}{(x^2+a^2)^{3/2}}\,dx \equiv -\frac{1}{a}\frac{\partial}{\partial a}\left[\int_{-\infty}^{\infty} \frac{e^{izx}}{(x^2+a^2)^{1/2}}\,dx\right] \equiv -\frac{1}{a}\frac{\partial B}{\partial a} \quad , \tag{2E.5}$$

where

$$B = \int_{-\infty}^{\infty} \frac{e^{izx}}{(x^2+a^2)^{1/2}}\,dx \equiv \int_{-\infty}^{\infty} \frac{\cos zx}{(x^2+a^2)^{1/2}}\,dx + i\int_{-\infty}^{\infty} \frac{\sin zx}{(x^2+a^2)^{1/2}}\,dx \quad . \tag{2E.6}$$

It is easily seen that the second integral in (2E.6) is zero. (Because the integral of an odd function from $-\infty$ to ∞ is zero). So (2E.6) becomes

$$B = \int_{-\infty}^{\infty} \frac{\cos zx}{(x^2+a^2)^{1/2}}\,dx \equiv 2\int_{0}^{\infty} \frac{\cos zx}{(x^2+a^2)^{1/2}}\,dx = 2K_0(az) \tag{2E.7}$$

where $K_0(az)$ is the modified Bessel function of second kind. Substituting (2E.7) into (2E.5) we get

$$A = -\frac{2}{a}\frac{\partial K_0(az)}{\partial a} = \frac{2z}{a}K_1(az), \tag{2E.8}$$

where $K_1(az)$ is the modified Bessel function of second kind. Substituting (2E.8) into (2E.3) we have

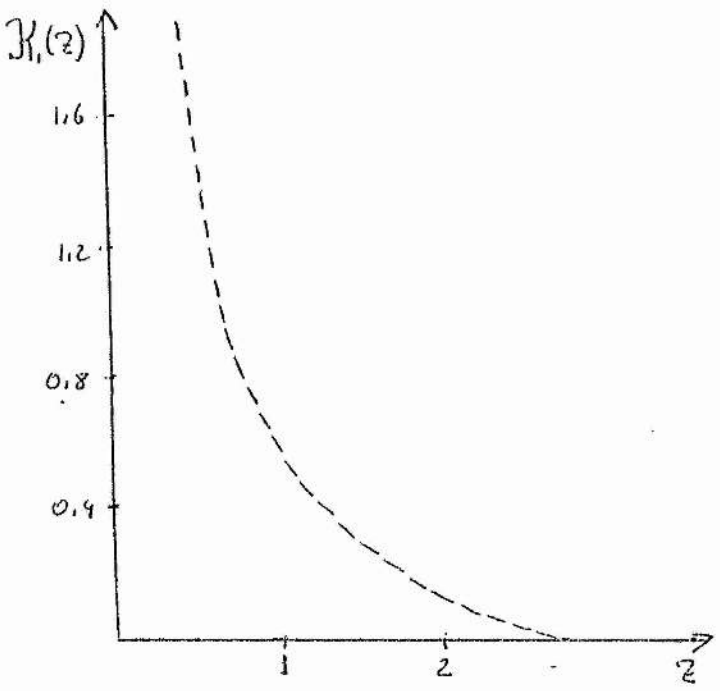
$$FT_2\left[\frac{1}{(\sigma^2+\lambda_3^2)^{3/2}}\right] = \int_{-\infty}^{\infty} dy\, e^{2\pi i y h_y}\frac{2z}{a}K_1(az). \tag{2E.9}$$

Substituting the value of z and a into (2E.9), it becomes

$$FT_2\left[\frac{1}{(\sigma^2+\lambda_3^2)^{3/2}}\right] = 4\pi h_x\int_{-\infty}^{\infty} dy\,\frac{e^{2\pi i y h_y}K_1\left[(y^2+\lambda_3^2)^{1/2}2\pi h_x\right]}{(y^2+\lambda_3^2)^{1/2}}. \tag{2E.10}$$

APPENDIX 2F

The behaviour of $K_1(z)$ function:



$$\lim_{z \to 0} K_\nu(z) = \frac{1}{2}\,\Gamma(\nu)\left(\frac{1}{2}z\right)^{-\nu}, \qquad (2F.1)$$

where $\Gamma(\nu)$ is the Gamma function. So

$$\lim_{z \to 0} K_1(z) = \frac{1}{2}\,\Gamma(1)\left(\frac{1}{2}z\right)^{-1} = \lim_{z \to 0} \frac{1}{z} \,. \qquad (2F.2)$$

APPENDIX 2G

Evaluation of W_q^P for Bravais lattices:

In this part we first calculate W_q^P for samples in the shape of a slab and a sphere then generalize the result with a theorem to any sample in the shape of a general ellipsoid of revolution.

A) Evaluation of W_q^P for a slab:

Consider the general expression (2.4-3) for W_q^P:

$$W_q^P = -e \sum_{q' \neq q} \frac{p \cdot (q - q')}{|q - q'|^3} \tag{2G.1}$$

and construct the fictitious Lorentz sphere concentric with the point q. The radius, R of the sphere must be chosen sufficiently large that we can make continuum approximation outside it. So the above summation can be split into two parts:

a) summation individually over the dipoles inside the Lorentz sphere

b) contribution from outside dipoles,

$$W_q^P = \underbrace{-e \sum_{q' \neq q} \frac{p \cdot (q - q')}{|q - q'|^3}}_{\text{(inside the Lorentz sphere)}} \underbrace{- e \sum_{q'} \frac{p \cdot (q - q')}{|q - q'|^3}}_{\text{(outside the Lorentz sphere)}} . \tag{2G.2}$$

Since we are dealing with Bravais lattices of equal and parallel dipoles it is easily seen that the first part of (2G.2) vanishes and one is left with

$$W_q^P = \underbrace{-e \sum_{q'} \frac{p \cdot (q - q')}{|q - q'|^3}}_{\text{(outside the Lorentz sphere)}} . \tag{2G.3}$$

As has been noted, the Lorentz sphere is chosen so that we can approximate the outside dipoles by a continuum. That is

$$W_q^P = -e \sum_{\substack{q' \\ (\text{outside the Lorentz sphere})}} \frac{\underset{\sim}{P}\cdot(\underset{\sim}{q}-\underset{\sim}{q}')}{|\underset{\sim}{q}-\underset{\sim}{q}'|^3} = -e \int_{V_1} \frac{\underset{\sim}{P}\cdot(\underset{\sim}{q}-\underset{\sim}{r}_1)}{|\underset{\sim}{q}-\underset{\sim}{r}_1|^3} dV_1 = -e \int_{V_1} \underset{\sim}{P}\cdot \underset{\underset{\sim}{r}_1}{\nabla} \frac{1}{|\underset{\sim}{q}-\underset{\sim}{r}_1|} dV_1 \qquad (2G.4)$$

or we can write*

$$W_q^P = -e \int_{V_1} \underset{\underset{\sim}{r}_1}{\nabla} \cdot \left(\frac{\underset{\sim}{P}}{|\underset{\sim}{q}-\underset{\sim}{r}_1|} \right) dV_1 \quad , \qquad (2G.5)$$

where V_1 is the volume of outside the sphere.

By the help of the Divergence theorem $\left(\int_V \nabla\cdot A\, dV = \int_S \underset{\sim}{A}\cdot\underset{\sim}{n}\, ds \right)$ (2G.5) can be written as

$$W_q^P = -e \int_{S_1} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{|\underset{\sim}{q}-\underset{\sim}{r}_1|} dS_1 \quad , \qquad (2G.6)$$

where S_1 is the surface of the volume V_1 and $\underset{\sim}{n}$ is the unit normal vector of S_1 .

From fig. (2.9)) it is seen that S_1 has two parts which are the inside surface, S_i and the outside surface, S_o . Therefore (2G.6) can be written as

$$W_q^P = -e \int_{S_1} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{|\underset{\sim}{q}-\underset{\sim}{r}_1|} dS_i - e \int_{S_o} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{|\underset{\sim}{q}-\underset{\sim}{r}_1|} dS_o \, . \qquad (2G.7)$$

---

*To write the Eq. (2G-5) we used the following vector identity:

$\underset{\sim}{\nabla}\cdot(\phi\underset{\sim}{A}) = \underset{\sim}{A}\cdot(\underset{\sim}{\nabla}\phi) + \phi(\underset{\sim}{\nabla}\cdot\underset{\sim}{A})$, in our case $\underset{\sim}{A} = \underset{\sim}{P}$ with $\underset{\sim}{\nabla}\cdot\underset{\sim}{P} = 0$ and $\phi = \frac{1}{|\underset{\sim}{q}-\underset{\sim}{r}_1|}$.

It is easily seen that the first part of (2G.7) vanishes:

$$\int_{S_i} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{|g-r_1|}\,dS_i = \int_0^{\pi} \frac{P\cos\theta}{R}\,2\pi R\sin\theta\, R\,d\theta = 0$$

and (2G.7) becomes

$$W_g^P = -e\int_{S_0} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{|g-r_1|}\,dS_0 \quad . \tag{2G.8}$$

From fig. (2.9) it is seen that (2G.8) can be written as

$$W_g^P = -e\int_{\text{plane (b)}} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}_b}{|\underset{\sim}{g}-\underset{\sim}{r}_1|_b}\,dS_b - e\int_{\text{plane(a)}} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}_a}{|\underset{\sim}{g}-\underset{\sim}{r}_1|_a}\,dS_a \quad , \tag{2G.9}$$

where

$$dS_a = 2\pi S\,dS \quad ,$$

$$dS_b = 2\pi S\,dS \quad ,$$

$$|\underset{\sim}{g}-\underset{\sim}{r}_1|_b = \sqrt{B^2+S^2} \quad ,$$

$$|\underset{\sim}{g}-\underset{\sim}{r}_1|_a = \sqrt{A^2+S^2} \quad ,$$

$$\underset{\sim}{P}\cdot\underset{\sim}{n}_b = P \quad ,$$

$$\underset{\sim}{P}\cdot\underset{\sim}{n}_a = -P \quad .$$

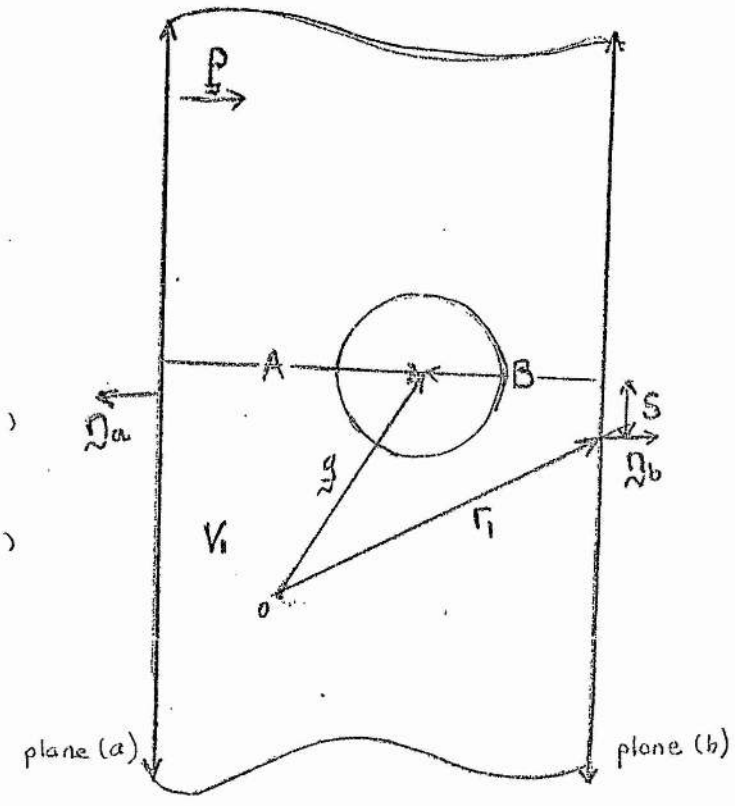


Figure (2.9)

With the above identities Eq. (2G.9) becomes

$$W_g^P = -e P \int_0^S \frac{2\pi S\, dS}{\sqrt{S^2+B^2}} + e P \int_0^S \frac{2\pi S\, dS}{\sqrt{S^2+A^2}} \qquad (2G.10)$$

or

$$W_g^P = -2\pi e P\left[A - B + S\left(1+\frac{B^2}{S^2}\right)^{1/2} - S\left(1+\frac{A^2}{S^2}\right)^{1/2}\right], \qquad (2G.11)$$

where S is the size of the slab.

For an infinite slab, where $S \gg A, B$; W_g^P becomes

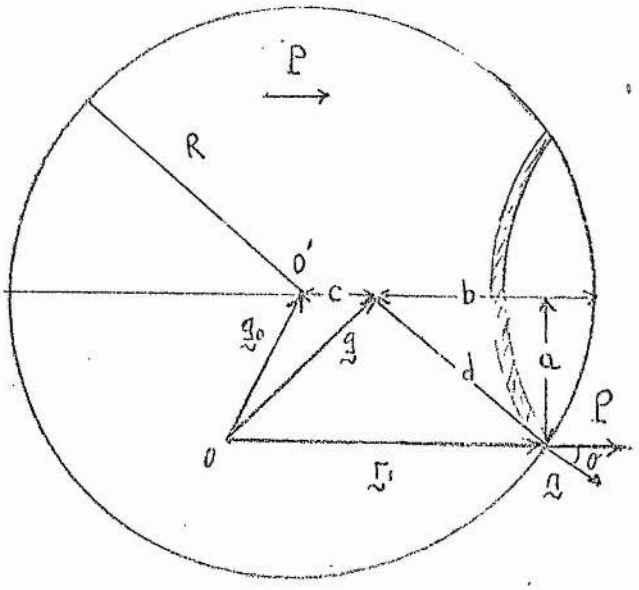
$$W_g^P = -2\pi e P (A-B) \qquad (2G.12)$$

or

$$W_g^P = e \underset{\sim}{E}_1 \cdot (\underset{\sim}{g} - \underset{\sim}{g}_0), \qquad (2G.13)$$

where $\underset{\sim}{g}_0$ is the vector going to the centre of mass.

B) Evaluation of W_g^P for a sphere:



$$dS_0 = 2\pi R^2 \sin\theta\, d\theta$$

$$P \cdot n = P\cos\theta$$

$$|\underset{\sim}{g} - \underset{\sim}{g}_0| = c$$

$$|\underset{\sim}{g} - \underset{\sim}{r}_1| = d = \sqrt{a^2+b^2} = \sqrt{R^2+c^2-2Rc\cos\theta}$$

Figure (2.10)

It is noted that (2G.8) is in fact a general result for a specimen in the shape of a general ellipsoid of revolution. So to calculate W_j^P for a sphere we can use (2G.8) again:

$$W_j^P = -e \int_{S_0} \frac{\underset{\sim}{P} \cdot \underset{\sim}{n}}{|\underset{\sim}{q} - \underset{\sim}{\Sigma}|} dS_0 \quad , \tag{2G.14}$$

or

$$W_j^P = -e \int_0^\pi \frac{P \cos\theta \, 2\pi R^2 \sin\theta \cdot d\theta}{\sqrt{R^2 + c^2 - 2Rc\cos\theta}} = -e \frac{4\pi}{3} P c \quad . \tag{2G.15}$$

From fig. (2.10)it is seen that (2G.15) can be written in the form

$$W_j^P = e \underset{\sim}{E}_1 \cdot (\underset{\sim}{q} - \underset{\sim}{q}_0) \quad , \tag{2G.16}$$

where $\underset{\sim}{q}_0$ is the vector going to centre of the sphere (centre of mass).

The results found in (2G.13) and (2G.16) imply that for a sample in the shape of a general ellipsoid of revolution W_j^P will have a unique form which is $e \underset{\sim}{E}_1 \cdot (\underset{\sim}{q} - \underset{\sim}{q}_0)$.

C) Theorem: For a sample in the shape of a general ellipsoid of revolution W_j^P has the form:

$$W_j^P = e \underset{\sim}{E}_1 \cdot (\underset{\sim}{q} - \underset{\sim}{q}_0) \quad , \tag{2G.17}$$

where $\underset{\sim}{E}_1$ is the depolarization field and $\underset{\sim}{q}_0$ is the vector going to the centre of mass.

Proof: Let us consider (2G.8) again;

$$W_q^P = -e \int_{S_0} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{|\underset{\sim}{q}-\underset{\sim}{r}|} dS_0 \quad .$$

The above formula is a general result as long as the uniform polarization exists. It applies to any sample in the shape of general ellipsoid of revolution. Let us write

$$W_q = -e\,\phi(\underset{\sim}{q}) \quad , \tag{2G.18}$$

where

$$\phi(\underset{\sim}{q}) = \int_{S_0} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{|\underset{\sim}{q}-\underset{\sim}{r}|} dS_0 \quad . \tag{2G.19}$$

Let us replace $\underset{\sim}{q}$ by a general vector, $\underset{\sim}{r}$ in (2G.19);

$$\phi(r) = \int_{S_0} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{|\underset{\sim}{r}-\underset{\sim}{r}_1|} dS_0 \quad . \tag{2G.20}$$

If we compare (2G.20) with (1.7) of Chapter I, we see that (2G.20) is the potential from which the depolarization field, $\underset{\sim}{E}_1$ is derived:

$$-\underset{\sim}{\nabla}_r \phi(r) = \underset{\sim}{E}_1(r) \tag{2G.21}$$

or

$$-\underset{\sim}{\nabla}_r \left[\int_{S_0} \frac{\underset{\sim}{P}\cdot\underset{\sim}{n}}{|\underset{\sim}{r}-\underset{\sim}{r}_1|} dS_0 \right] = \underset{\sim}{E}_1(r) \quad . \tag{2G.22}$$

The depolarization field, $\underset{\sim}{E}_1(r)$ has an advantageous property for specimens in the shape of a general ellipsoid of revolution (a class that includes spheres, cylinders and discs). This property is

"A uniform polarization produces a uniform depolarization field. So for a sample in the shape of a general ellipsoid of revolution $\underset{\sim}{E}_1(r)$ will be uniform."

$$\underset{\sim}{E}_1(r) = \underset{\sim}{E}_1 \,. \tag{2G.23}$$

Substitution of (2G.23) into (2G.21) gives

$$-\nabla_r \phi(r) = \underset{\sim}{E}_1 \,, \tag{2G.24}$$

or

$$\phi(r) = -\underset{\sim}{E}_1 \cdot \underset{\sim}{r} + C \,. \tag{2G.25}$$

Now we replace $\underset{\sim}{r}$ with $\underset{\sim}{q}$ in (2G.25);

$$\phi(q) = -\underset{\sim}{E}_1 \cdot \underset{\sim}{q} + C \,. \tag{2G.26}$$

From the boundary conditions we find,

$$C = \underset{\sim}{E}_1 \cdot \underset{\sim}{q}_0 \,, \tag{2G.27}$$

where $\underset{\sim}{q}_0$ is the point where $\phi(q)$ becomes zero. For uniform polarization $\underset{\sim}{q}_0$ would be the centre of mass. Substituting (2G.27) into (2G.26) gives

$$\phi(q) = -\underset{\sim}{E}_1 \cdot \underset{\sim}{q} + \underset{\sim}{E}_1 \cdot \underset{\sim}{q}_0 = -\underset{\sim}{E}_1 \cdot (\underset{\sim}{q} - \underset{\sim}{q}_0) \,. \tag{2G.28}$$

And W_q^f becomes

$$W_q^f = -e\,\phi(q) = e\,\underline{E}_1 \cdot (\underline{q} - \underline{q}_0) \quad . \tag{2G.29}$$

CHAPTER III

THE QUESTION OF THE LOCAL CORRECTION TO THE HALL MOBILITY OF THE SMALL POLARON

3.1 Review of the Hall mobility of the small polaron:

The existence of a Hall effect of the small polaron for a non-polar crystal was first considered by Friedman and Holstein[19]. The model is a suitable generalization of the one-dimensional molecular-crystal model. The generalizations are as follows:

Since the existence of the Hall effect needs more than one spatial dimension, one can generalize equation (2.2) to the three-dimensions in the following sense: Although the molecular crystal is taken to be three-dimensional, the motion of the electron occurs in a plane which is perpendicular to the applied magnetic field, $\underset{\sim}{H}$. One replaces the scalar site index n by a vector index; $\underset{\sim}{q} = \sum_{i=1}^{3} q_i \underset{\sim}{a}_i$, where the $\underset{\sim}{a}_i$ are a basic set of lattice displacement vectors and the q_i are integers.

Secondly, the effect of a constant applied electric field, $\underset{\sim}{E}_0$, and applied magnetic field, $\underset{\sim}{H}$, must be included in the Hamiltonian. The effect of the magnetic field is to modify the local wave functions $\phi(\underset{\sim}{r}-\underset{\sim}{q}, x_q)$ to new local functions $\phi_q(\underset{\sim}{r}, x_q)$ which satisfy the equation

$$\left[\frac{1}{2m}\left(\frac{\hbar}{i}\underset{\sim}{\nabla}_r + \frac{e\underset{\sim}{A}}{c}\right)^2 + U(\underset{\sim}{r}-\underset{\sim}{q}, x_q)\right]\phi_q(\underset{\sim}{r}, x_q) = E(x_q)\,\phi_q(\underset{\sim}{r}, x_q), \tag{3.1}$$

where the "symmetrical" gauge is taken

$$\underset{\sim}{A} = \frac{1}{2}\left[\underset{\sim}{H} \times \underset{\sim}{r}\right].$$

Now by introducing the gauge transformation

$$\phi_g(r, X_g) = \chi_g(r, X_g)\, e^{-ie[H \times g]\cdot r / 2\hbar c} \tag{3.2}$$

the equation (3.1) can be written as

$$\left[\frac{1}{2m}\left(\frac{\hbar}{i}\nabla_r + \frac{e}{2c} H \times (r-g)\right)^2 + U(r-g)\right]\chi_g(r) = E(X_g)\chi_g(r)\,, \tag{3.3}$$

the solution of which are of the form

$$\chi_g(r) = \chi(r-g)\,. \tag{3.4}$$

It is noted that, to first order in H, equation (3.1) can be written as

$$\left[-\frac{\hbar^2}{2m}\nabla_r^2 + \frac{eH}{2mc}\ell_z + U(r-g, X_g)\right]\chi_g(r) = E(X_g)\chi_g(r)\,. \tag{3.5}$$

On the other hand, since the basic wave functions, $\phi(r-g, X_g)$, are assumed to be non-degenerate, hence real, they will be Σ-states $(\ell_z = 0)$, i.e., $\ell_z \phi(r-g, X_g) = 0$. Therefore they will satisfy the following equations:

$$\left[-\frac{\hbar^2}{2m}\nabla_r^2 + \frac{eH}{2mc}\ell_z + U(r-g, X_g)\right]\phi(r-g, X_g) = E(X_g)\phi(r-g, X_g)\,. \tag{3.6}$$

Now comparing (3.5) and (3.6) one can say that $\chi_g(r)$ is equal to $\phi(r-g, X_g)$ to first order in H. One thus has

$$\phi_g(r, X_g) = \phi(r-g, X_g)\, e^{-ie[H \times g]\cdot r / 2\hbar c}\,. \tag{3.7}$$

Following the same analysis of Appendix I of reference (16) with the new local function $\phi_g(r, X_g)$, the modified transfer integral can be calculated. It takes the form

$$J(H) = -J\, e^{i\alpha_{g,g+h}} \qquad (3.8)$$

where

$$J = \int \phi(r)\, U(r)\, \phi(r-h)\, dV \qquad (3.9)$$

and

$$\alpha_{g,g+h} = -\frac{e}{2\hbar c}\left[H\cdot(h\times g)\right] = -\frac{e}{\hbar c}\, H\cdot A_{g,g+h} \qquad (3.10)$$

with

$$A_{g,g+h} = \frac{1}{2}\left|h\times g\right| = \frac{1}{2}\left|(g+h)\times g\right| \qquad (3.11)$$

which is the area of the triangle whose vertices coincide with the site g, $g+h$ and the origin. It may be mentioned in passing that, although the magnetic phase factors $\alpha_{g,g'}$ are not uniquely defined (because the origin is chosen arbitrarily), the sum of the phase factors linking any set of three (or more) sites in a closed cycle is unique; for example:

$$\alpha_{g_3,g_2} + \alpha_{g_2,g_1} + \alpha_{g_1,g_3} = -\frac{e}{\hbar c}\, H\cdot A_{321}\,, \qquad (3.12)$$

where

$$A_{321} = \frac{1}{2}\left[(g_1\times g_2) + (g_2\times g_3) + (g_3\times g_1)\right] \qquad (3.13)$$

is the area vector of the triangle whose vertices coincide with the sites g_1, g_2, g_3. Equation (3.12) is crucial to the existence of a non-vanishing Hall effect.

The third generalization of (2.2) involves taking into account the existence of a spatially constant dc electric field, E.

To do so one adds the standard electric field term ,

$$H^{(E)} = e \underset{\sim}{E}_0 \cdot \underset{\sim}{\mathcal{L}} ,$$

to the total Hamiltonian. In this process $H^{(E)}$ automatically separates into two parts. One of these, namely $e \underset{\sim}{E}_0 \cdot \underset{\sim}{\mathcal{L}}$, appears as an additive modification of the local site energy term, $A X_g$. The other, $e \underset{\sim}{E}_0 \cdot (\underset{\sim}{\mathcal{L}} - \underset{\sim}{g})$, gets included in the local site Hamiltonian of equation (2.2) of chapter II. For zero'th order wave functions which are non-degenerate, spherically symmetric, Σ-states, this extra term results in no first order change of the wavefunctions. Therefore to the first order, $\phi(r - g, X_g)$ remain unchanged*.

The results of the above-discussed three generalizations can be summarized by writing down the equation obeyed by the coefficients $a_g(\cdots X_g \cdots)$ of the total wavefunction:

$$i\hbar \frac{\partial a_g}{\partial t} = (H_L - A X_g + e \underset{\sim}{E}_0 \cdot \underset{\sim}{g}) a_g - J \sum_{\underset{\sim}{h}} a_{g+h} e^{i \alpha_{g, g+h}} . \tag{3.14}$$

Equation (3.14) constitutes the basis of the study of the Hall effect for a non-polar crystal.

Now, if we compare equation (3.14) with equation (2.14) of chapter II we can say that in the presence of the applied magnetic field the only change is that the transfer integral $-J$ is replaced with a magnetic field-dependent transfer integral $-J e^{i \alpha_{g, g+h}}$:

$$-J \longrightarrow -J e^{i \alpha_{g, g+h}} . \tag{3.15}$$

*See for example, reference 38 p.159

3.1a The Hall effect in the site jump regime:

As was mentioned in chapter II, for temperatures above the critical temperature $\left(\sim \frac{1}{2}\,\Theta_0\right)$ the small polaron motion occurs by means of thermally activated jumps from one local site $\underset{\sim}{g}$ to a neighbouring site $\underset{\sim}{g}'$ by virtue of the non-vanishing transfer integral J . The jump rate, ω_T^0 , at high temperatures , $T > \Theta_0$, takes the form of an activated process :

$$\omega_T^0(g \to g') = \frac{J^2}{\hbar}\left[\frac{\pi}{4kTE_a}\right]^{1/2} e^{-E_a/kT} \tag{3.16}$$

which is proportional to J^2 .

In the presence of the applied magnetic field the above jump rate takes the form

$$\omega_T''(g \to g+h) = \frac{|Je^{i\alpha_{g,g+h}}|^2}{\hbar}\left[\frac{\pi}{4kTE_a}\right]^{1/2} e^{-E_a/kT} \tag{3.17}$$

which is independent of $\underset{\sim}{H}$. Therefore in treating the Hall effect, higher order processes involving the occupation of (at least) three sites must be taken into account. Thus the elementary transition probabilities must be calculated for three mutually near neighbouring sites. The simple case is a two-dimensional triangular geometry which was first considered by Friedman and Holstein[19]. In this geometry three sites of this array form an equilateral triangle: they are labelled simply 1 , 2 and 3 as in figure (3.1). In this geometry the electron is taken to be initially located, let us say, on site 1 . When a simultaneous coincidence in the electronic energy of the three sites $\left(-A\chi_1 = -A\chi_2 = -A\chi_3\right)$ occurs,

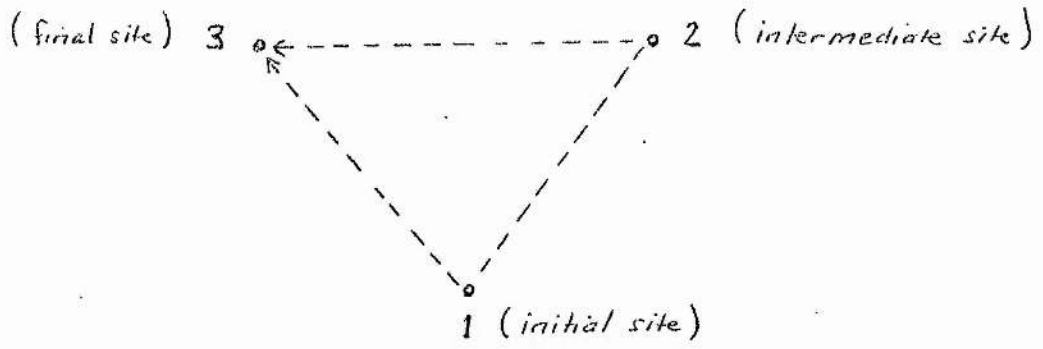


Figure (3.1): Triangular site geometry and the Interference Mechanism

the total transition amplitude, for example, at site 3 is the sum of the first order amplitude corresponding to a direct jump from 1 to 3 , and the second order amplitude involving intermediate occupancy of site 2 and the interference terms. This leads to a net contribution (at site 3) proportional in sign and magnitude to the enclosed magnetic flux, $\underset{\sim}{H} \cdot \underset{\sim}{A}_{321}$, hence to the applied magnetic field $\underset{\sim}{H}$. The magnetic field induced components of the jump rates corresponding to the above processes are calculated in reference (19). It was first calculated by a classical occurrence probability approach which treats the lattice vibrational coordinates classically. Then by a full quantum mechanical approach. Both results agree with each other in the classical limit $(T \gg \Theta_D)$ and take the form

$$\omega_3^{(H,E_0)}(1\to 2\to 3) = \omega_3^{(H)} \exp\left[e\,\underset{\sim}{E}_0 \cdot \left[\underset{\sim}{h}_{31} + \underset{\sim}{h}_{21}\right]/3kT\right] , \tag{3.18}$$

where

$$\omega_3^{(H)} = \left(\frac{e\,\underset{\sim}{H}\cdot\underset{\sim}{A}_{321}}{\hbar c}\right)\frac{I^3}{\hbar}\,\frac{2\pi}{3\sqrt{3}\,kT\varepsilon_3}\,e^{-\varepsilon_3/kT} , \tag{3.19}$$

$$\underset{\sim}{h}_{ij} = \underset{\sim}{q}_j - \underset{\sim}{q}_i$$

and $\mathcal{E}_3$ is the activation energy corresponding to an energetical coincidence of three sites which is found to be 4/3 times the activation energy corresponding to an energetical coincidence of two sites:

$$\mathcal{E}_3 = \frac{4}{3} E_a \,. \tag{3.20}$$

Finally it is noted that the total transition amplitude at site 2 is the sum of first order amplitude $1 \to 2$ and the second order amplitude $1 \to 3 \to 2$ and the interference terms. This leads to a net contribution at site 2 proportional in sign and magnitude to the enclosed magnetic flux, $H \cdot A_{231}$ which is opposite to that of at site 3. As a result there will be a net transverse Hall current in the direction $2 \to 3$. This property leads to a non-vanishing Hall mobility of the small polaron.

THE HALL MOBILITY OF THE SMALL POLARON OF A POLARIZABLE DIELECTRIC IN THE SITE JUMP REGIME

3.2a Derivation of fundamental equation for Hall effect:

In this section we first derive the basic equation for the study of the Hall effect of the small polaron in a polarizable dielectric, then calculate the field modified jump rates.

In section (2.3a) we derived the basic equation of motion for the case of a polarizable dielectric in the presence of an applied field, E_o . The equations for the coefficients were found to take the form

$$i\hbar \frac{\partial a_g}{\partial t} = \left[H_L - A\chi_g + e\underset{\sim}{E}_o \cdot \underset{\sim}{g} + W_g^{\rho} \right] - J \sum_{\underset{\sim}{h}} a_{g+h} \qquad (3.2\text{-}1)$$

with

$$W_g^{\rho} = \int dV \, |\phi(\underset{\sim}{r} - \underset{\sim}{g}, \chi_g)|^2 \sum_{\underset{\sim}{g}' \neq \underset{\sim}{g}} \frac{-e\,\underset{\sim}{g}\cdot(\underset{\sim}{r} - \underset{\sim}{g}')}{|\underset{\sim}{r} - \underset{\sim}{g}'|^3} .$$

To study the Hall effect, equation (3.2-1) must be generalized to take into account of the effect of an applied magnetic field, $\underset{\sim}{H}$ which is assumed to be perpendicular to the electric field, $\underset{\sim}{E}_o$. As was discussed in the introduction, the effect of the applied magnetic field in first order is just to replace the transfer integral $-J$ by the magnetic field dependent one, namely $-J e^{i\alpha_{g,g+h}}$, where $\alpha_{g,g+h}$ is given by (3.d0). Therefore in the presence of the applied magnetic field equation (3.2-1) reads .

$$i\hbar \frac{\partial a_g}{\partial t} = \left[H_L - A\chi_g + e\underset{\sim}{E}_o \cdot \underset{\sim}{g} + W_g^{\rho} \right] - J \sum_{\underset{\sim}{h}} a_{g+h} e^{i\alpha_{g,g+h}} . \qquad (3.2\text{-}2)$$

The assumptions discussed in the previous sections are explicitly employed here as well.

Equation (3.2-2) will form the basis for the study of the Hall effect for a polarizable dielectric.

It may here be remarked that, again, the only difference between (3.2-2) and (3.14) is the extra W_g^p term in the square bracket. The appearance of this term gives rise to possibility of local field type correction in the Hall effect of the small polaron.

As was discussed in the introduction, although the lowest order jump-rate is adequate in considering the polaron drift mobility, higher order processes, involving the occupation of (at least) three sites, must be taken into account in treating the Hall effect. We shall consider the simplest case which is a two-dimensional triangular geometry. As far as local field type correction is concerned this simple geometry will be adequate to study the Hall effect of the small polaron for a polarizable dielectric.

MAGNETIC AND ELECTRIC FIELD MODIFIED JUMP RATE FOR A POLARIZABLE DIELECTRIC

3.2b Classical occurrence-probability approach:

In this section we calculate the field (both magnetic and electric) induced components of the jump rate for a polarizable dielectric at high temperatures $(T \gg \Theta_D)$. The elementary transition probabilities will be calculated for the three mutually near neighbour site arrangement shown in figure (3.2).

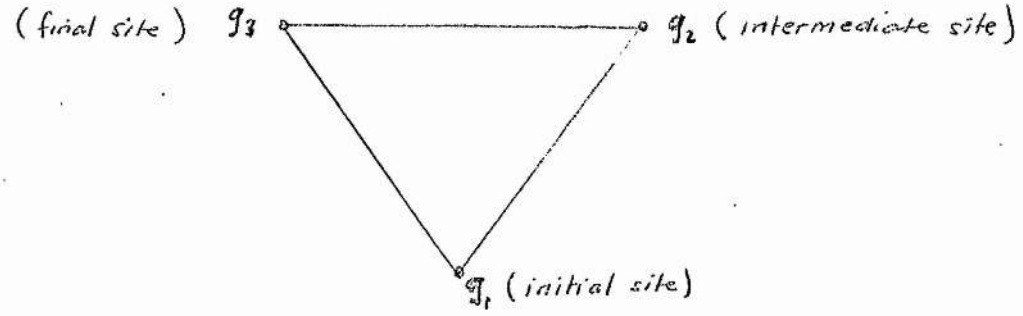


Figure 3.2: Elementary three-site configuration

We start with the set of equations:

$$i\hbar \frac{\partial a_q}{\partial t} = \left[-A X_q + e\underline{E}_0 \cdot \underline{r} + W_q^f \right] a_q - \sum_{h} a_{q+h}\, e^{i\alpha_{q,q+h}} \qquad (3.2\text{-}3)$$

which are obtained from (3.2-2) by omitting the vibrational Hamiltonian H_L. As was mentioned earlier in the classical occurrence-probability approach the lattice motion is treated classically; that is, each interatomic separation X_q is assumed to be a function of time, $X_q(t)$. In the classical occurrence probability approach the $X_q(t)$ are determined by

the Hamiltonian

$$H_{(initial)} = H_L - A\,X_{(initial)} \,. \tag{3.2-4}$$

Following the argument of reference (19), it will be convenient to drop the electric field terms from (3.2-3) it can be reinserted any time by adding it to the electronic energy as follows:

$$-A\,X_g \longrightarrow -A\,X_g + e\,\underset{\sim}{E}_0 \cdot \underset{\sim}{g} + W_g^P \tag{3.2-5}$$

or

$$X_g \longrightarrow X_g - \frac{e\,\underset{\sim}{E}_0 \cdot \underset{\sim}{g} + W_g^P}{A} \,. \tag{3.2-6}$$

At this point we shall begin to study the perturbation solution of the coupled set of equations (3.2-3) by noting that in the absence of the electronic transfer integral J, the solution for the electron localized on site $\underset{\sim}{g}_l$ is

$$a_l^{(0)} = e^{i\,\phi_l(t)} \,, \tag{3.2-7}$$

where

$$\phi_l(t) = \frac{A}{\hbar} \int_0^t X_l(t')\,dt' \,. \tag{3.2-8}$$

In the presence of non-vanishing (but small) J, one obtains the standard perturbation development for the occupation amplitudes of the other sites; in particular, for the three-site configuration of figure (3.2) one has

$$a_3^{(1)}(t) = -\frac{J}{i\hbar}\, e^{i\alpha_{31}}\, e^{i\phi_3(t)} \int_{-\frac{T}{2}}^{t} e^{i[\phi_1(t') - \phi_3(t')]}\,dt' \,. \tag{3.2-9}$$

$$a_3^{(2)}(t) = -\frac{J}{i\hbar} e^{i\alpha_{32}} e^{i\phi_3(t)} \int_{-\frac{T}{2}}^{t} a_2^{(1)}(t') e^{i\phi_3(t')} dt'$$

$$= -\frac{J^2}{\hbar^2} e^{i(\alpha_{32}+\alpha_{21})} e^{i\phi_3(t)} \int_{-\frac{T}{2}}^{t} dt' e^{i[\phi_2(t)-\phi_3(t')]} \int_{-\frac{T}{2}}^{t'} dt'' e^{i[\phi_1(t'')-\phi_2(t'')]}$$

(3.2-10)

where the superscripts (1) and (2) on $a_3^{(1)}$ and $a_3^{(2)}$ respectively refer to the fact that $a_3^{(1)}$ is the transition amplitude first order in J and $a_3^{(2)}$ is the transition amplitude second order in J.

The occupation probability $W_3(t)$ of site g_3 at time t is obtained by taking the absolute square of $|a_3^{(1)} + a_3^{(2)}|$:

$$W_3(t) = |a_3^{(1)} + a_3^{(2)}|^2 = |a_3^{(1)}|^2 + |a_3^{(2)}|^2 + a_3^{(1)*} a_3^{(2)} + a_3^{(1)} a_3^{(2)*}.$$

(3.2-11)

It is noted that $|a_3^{(1)}|^2$ and $|a_3^{(2)}|^2$ do not have any H-dependence. Therefore as far as the Hall effect is concerned, it is the interference terms alone that one is interested in. To the first order, we take the terms which are proportional to the magnetic field H : One then expands the $\exp(i\alpha_{ji})$ as power series in the α_{ji} and discards all terms except those linear in the α_{ji} . So one finds* the magnetic field-dependent contribution to the probability of occupation of site g_3 :

$$W_3^{(H)}\left(\frac{T}{2}\right) = \frac{\alpha J^3}{\hbar^3} \left[\left(\int_{-\frac{T}{2}}^{\frac{T}{2}} dt' e^{-i[\phi_1(t')-\phi_3(t')]} \right) \left(\int_{-\frac{T}{2}}^{\frac{T}{2}} dt' e^{i[\phi_2(t')-\phi_3(t')]} \right) \times \int_{-\frac{T}{2}}^{t'} dt'' e^{i[\phi_1(t'')-\phi_2(t'')]} \right) + \text{c.c.} \Bigg] \quad (3.2\text{-}12)$$

*We set $t = \frac{T}{2}$ so that the total time interval becomes T .

where $$\alpha = \alpha_{21} + \alpha_{32} + \alpha_{13} = \frac{e\,\underset{\sim}{H}\cdot\underset{\sim}{A}_{321}}{\hbar c} \cdot \qquad (3.2\text{-}13)$$

The evaluation of (3.2-12) is carried out in Appendix (3.A). The result is

$$W_3^{(H)} = \frac{\alpha J^3}{2\hbar^3} \exp\left(\frac{iA}{2\hbar} v_{12} \frac{v_{31}}{v_{23}} t_{12}^2\right)\left[\left(\frac{2\pi\hbar}{A|v_{12}|}\right)^{1/2} e^{\pm i\frac{\pi}{4}}\right]$$

$$\left[\left(\frac{2\pi\hbar}{A|v_{23}|}\right)^{1/2} e^{\pm i\frac{\pi}{4}}\right]\left[\left(\frac{2\pi\hbar}{A|v_{31}|}\right)^{1/2} e^{\pm i\frac{\pi}{4}}\right] + c.c.) \qquad (3.2\text{-}14)$$

where v_{ij} is the relative velocity between sites i and j i.e., $v_{ij} = v_i - v_j$ and t_{12} is the time within the interval $-\frac{T}{2}$ to $\frac{T}{2}$ at which a coincidence of sites 1 and 2 takes place.

In order to obtain the jump rate, equation (3.2-14) must be multiplied by the mean probability for a coincidence of X_1 and X_3 at time $t_{31}\,(=0)$ with relative velocity between v_{31} and $v_{31} + dv_{31}$, and a coincidence of X_1 and X_2 occurring between times t_{12} and $t_{12} + dt_{12}$ with relative velocity between v_{12} and $v_{12} + dv_{12}$. This occurrence probability is denoted by $P_T^c(v_{31}, v_{21}, t_{12})\,dv_{31}\,dv_{12}\,dt_{12}$. Subsequently integrations over v_{31}, v_{12} and t_{12} gives the jump rate:

$$\omega_3^{(H)} = \iiint dv_{31}\,dv_{12}\,dt_{12}\,W_3^{(H)}\,P_T^c(v_{31}, v_{12}, t_{12}), \qquad (3.2\text{-}15)$$

where $$P_T^c(v_{31}, v_{12}, t_{12})\,dv_{31}\,dv_{12}\,dt_{12} =$$

$$\bar{Z}^{-1}\int\cdots\int dx_1\cdots dx_N\,dv_1\cdots dv_N \exp\left[-\frac{H_L + H_{int}}{kT}\right]$$

$$\times\,\delta[x_3(0) - x_1(0)]\,|v_{31}|\,dt_{31}\,\delta[v_3(0) - v_1(0) - v_{31}]\,dv_{31}$$

$$\times\,\delta[x_2(t_{12}) - x_1(t_{12})]\,|v_{12}|\,dt_{12}\,\delta[v_2(t_{12}) - v_1(t_{12}) - v_{12}]\,dv_{12}$$

(3.2-16)

with $\bar{Z}$ being the vibrational partition function.

As was discussed in section (2.3-6), to include the effect of electric field and its induced effect in the transition rate, we assume that the electric field and its induced effects enter into the occurrence probability in that one looks for coincidence of the electronic plus electric field energies of neighbouring sites. Therefore in (3.2-16) we replace

$$\delta(x_g - x_{g'}) \longrightarrow \delta\left[x_g - x_{g'} - \frac{eE_0\cdot(g-g') + (W_g^f - W_{g'}^f)}{A}\right]. \tag{3.2-17}$$

In Appendix 3B we calculate the modification of the occurrence probability for this three-site coincidence event in the presence of the applied electric field and its induced effect. The corresponding occurrence probability is given by (3B.14) and is quoted here for convenience:

$$P_T^c(E, v_{31}, v_{12}, t_{12}) = e^{\frac{1}{3kT}\left[eE_0\cdot(g_1-g_3) + (W_{g_1}^f - W_{g_3}^f) + eE_0\cdot(g_1-g_2) + (W_{g_1}^f - W_{g_2}^f)\right]} \times P_T^c(v_{31}, v_{12}, t_{12}). \tag{3B.14}$$

Then from (3.2-15) and (3B.14) the field modified jump-rate for a polarizable dielectric takes the form

$$\omega_3^{(H,E)} = e^{\frac{1}{3kT}\left[eE_0\cdot(g_1-g_3) + (W_{g_1}^f - W_{g_3}^f) + eE_0\cdot(g_1-g_2) + (W_{g_1}^f - W_{g_2}^f)\right]} \omega_3^{(H)}. \tag{3.2-18}$$

If we compare (3.2-18) with (3.18) we see that investigation of the local field correction to Hall mobility of the small polaron reduces to evaluation of the terms $(W_{g_1}^f - W_{g_3}^f)$ and $(W_{g_1}^f - W_{g_2}^f)$ for three mutually near neighbouring sites. Applying the results of section (2.4) we can write that

$$W^{f}_{q_1} - W^{f}_{q_3} = e\,\underline{E}_1 \cdot (\underline{q}_1 - \underline{q}_3) \tag{3.2-19}$$

$$W^{f}_{q_1} - W^{f}_{q_2} = e\,\underline{E}_1 \cdot (\underline{q}_1 - \underline{q}_2) . \tag{3.2-20}$$

Substitution of (3.2-19) and (3.2-20) into (3.2-18) gives

$$\omega_3^{(H,E)} = e^{\frac{1}{3kT}\left[e\,\underline{E}_{mac}\cdot(\underline{q}-\underline{q}_3) + e\,\underline{E}_{mac}\cdot(\underline{q}_1-\underline{q}_2)\right]} \omega_3^{(H)} . \tag{3.2-21}$$

From (3.2-21) it is noted that the net electric field appearing in the jump rate and hence in the Hall mobility is simply equal to the macroscopic field, $\underline{E}_{mac}$.

As was pointed out in section (2.4) the above result, namely the absence of local field correction to the Hall mobility is obtained on the basis of the assumption that all sites are crystallographically equivalent. However it does not apply to those cases of inequivalent sites. In this case (3.2-19) and (3.2-20), in accordance with (2.4-45), become

$$W^{f}_{q_1} - W^{f}_{q_3} = e\,\underline{E}_1 \cdot (\underline{q}_1 - \underline{q}_3) + e\,(\underline{E}^{q_1}_3 - \underline{E}^{q_3}_3) \cdot (\underline{q}_1 - \underline{q}_3) \tag{3.2-22}$$

and

$$W^{f}_{q_1} - W^{f}_{q_2} = e\,\underline{E}_1 \cdot (\underline{q}_1 - \underline{q}_2) + e\,(\underline{E}^{q_1}_3 - \underline{E}^{q_2}_3) \cdot (\underline{q}_1 - \underline{q}_2) \tag{3.2-23}$$

which result in local field type corrections to the Hall mobility.

3.3 Application of the present theory to the glasses:

In section (2.6) we argued that to apply the present theory to the studied glasses, we introduce the following generalizations:

A) In the absence of the magnetic field the non-degenerate local wave functions are taken to be 3d-states.

B) The summation over periodic lattices are replaced by summations over the random lattices.

In this section we investigate the possible effect of the generalization (A) to the Hall mobility of the small polaron. First recall the equation (3.I):

$$\left[-\frac{1}{2m}\left(\frac{\hbar}{i}\nabla_r + \frac{eA}{c}\right)^2 + U(r-q)\right]\phi_q(r) = E\,\phi_q(r) \quad , \tag{3.3-1}$$

and by introduction of the gauge transformation

$$\phi_q(r) = \chi_q(r)\, e^{-\frac{ie[H\times q]\cdot r}{2\hbar c}} \quad , \tag{3.3-2}$$

$$\left[\frac{1}{2m}\left(\frac{\hbar}{i}\nabla_r + \frac{eH\times(r-q)}{2c}\right) + U(r-q)\right]\chi_q(r) = E\,\chi_q(r) \quad , \tag{3.3-3}$$

with the solution of the form

$$\chi_q(r) = \chi_q(r-q) \quad . \tag{3.3-4}$$

To first order in the magnetic field, (3.3-3) can be written in the following form :

$$\left[-\frac{\hbar^2}{2m}\nabla_r^2 + \frac{eH\ell_z}{2mc} + U(r-q)\right]\chi_q(r) = E\,\chi_q(r) \quad , \tag{3.3-5}$$

where ℓ_z is the z component of the angular momentum operator.

*Here the magnetic field is assumed to be in the z direction.

As a result of the generalization (A), the zero-field wave functions are assumed to be one of the following real 3d wave functions, namely

$$\phi_1 = xy\, f(r) = f(r)\,\frac{1}{i\sqrt{2}}\left(Y_{2,2} - Y_{2,-2}\right)$$

$$\phi_2 = yz\, f(r) = -f(r)\,\frac{1}{i\sqrt{2}}\left(Y_{2,1} + Y_{2,-1}\right)$$

$$\phi_3 = zx\, f(r) = -f(r)\,\frac{1}{\sqrt{2}}\left(Y_{2,1} - Y_{2,-1}\right)$$

$$\phi_4 = (z^2 - x^2)\, f(r) = f(r)\left[\frac{Y_{2,0}}{2} - \frac{1}{\sqrt{2}}\left(Y_{2,2} + Y_{2,-2}\right)\right]$$

$$\phi_5 = (x^2 - y^2)\, f(r) = f(r)\,\frac{1}{\sqrt{2}}\left(Y_{2,2} + Y_{2,-2}\right) .$$

Assume that $\phi_1 = xy\, f(r)$ corresponds to the ground state of an octahedral site and $\phi_5 = (x^2 - y^2) f(r)$ corresponds to the ground state of a tetrahedral site (c.f. figure (2.13)). If $\underset{\sim}{q}$ is an octahedral site, in the absence of the magnetic field, (3.3-5) becomes

$$\left[-\frac{\hbar^2}{2m}\nabla_r^2 + U(\underset{\sim}{r} - \underset{\sim}{q})\right]\phi_1 = E\,\phi_1 \qquad (3.3\text{-}6)$$

i.e.,

$$\chi_{\underset{\sim}{q}}^{(0)} = \phi_1 .$$

To first order in $\underset{\sim}{H}$ the perturbative solution of $\chi_{\underset{\sim}{q}}$ is

$$\chi_{\underset{\sim}{q}} = \phi_1 + i b H \phi_5 \qquad (3.3\text{-}7)$$

where b is a real constant. Substitution of (3.3-7) into (3.3-5) gives

$$\phi_{\underset{\sim}{q}}(r) = \left[\phi_1 + i b H \phi_5\right] e^{\frac{-ie\left[\underset{\sim}{H}\times\underset{\sim}{q}\right]\cdot\underset{\sim}{r}}{2\hbar c}} . \qquad (3.3\text{-}8)$$

Similarly if $\underset{\sim}{g}$ is a tetrahedral site, the solution of (3.3-5) to the first order in $\underset{\sim}{H}$ reads

$$\phi_g(r) = \left[\phi_s - ibH\,\phi_i\right] e^{\frac{-ie[\underset{\sim}{H}\times\underset{\sim}{g}]\cdot\underset{\sim}{r}}{2\hbar c}}. \tag{3.3-9}$$

The next thing is to consider the modification of $J_{g,g+h}$:

a) Assume that $\underset{\sim}{g}$ and $\underset{\sim}{g'}=\underset{\sim}{g}+\underset{\sim}{h}$ are two nearest octahedral sites:

$$J_{g,g+h} = \int \phi_i^*(\underset{\sim}{r}-\underset{\sim}{g})\,\phi_i(\underset{\sim}{r}-\underset{\sim}{g}-\underset{\sim}{h})\,U(\underset{\sim}{r}-\underset{\sim}{g})\,e^{-\frac{ie[\underset{\sim}{h}\times\underset{\sim}{H}]\cdot\underset{\sim}{r}}{2\hbar c}}; \tag{3.3-10}$$

substituting the value of $\phi_i(\underset{\sim}{r}-\underset{\sim}{g})$ from (3.3-8) we can write

$$J_{g,g+h} = \int\left[\phi_i(\underset{\sim}{r}-\underset{\sim}{g})+ibH\,\phi_s(\underset{\sim}{r}-\underset{\sim}{g})\right]^*\left[\phi_i(\underset{\sim}{r}-\underset{\sim}{g}-\underset{\sim}{h})+ibH\,\phi_s(\underset{\sim}{r}-\underset{\sim}{g}-\underset{\sim}{h})\right]$$
$$\times\, U(\underset{\sim}{r}-\underset{\sim}{g})\, e^{\frac{-ie[\underset{\sim}{H}\times\underset{\sim}{h}]\cdot\underset{\sim}{r}}{2\hbar c}}\, dV\,. \tag{3.3-11}$$

Transforming the integration variable to $\underset{\sim}{\rho} = \underset{\sim}{r}-\underset{\sim}{g}-\frac{\underset{\sim}{h}}{2}$ and expanding the exponent about $\underset{\sim}{\rho}=0$ to terms linear in $\underset{\sim}{H}$, one has

$$J_{g,g+h} = \int\left[\phi_i(\underset{\sim}{\rho}+\frac{\underset{\sim}{h}}{2})-ibH\,\phi_s(\underset{\sim}{\rho}+\frac{\underset{\sim}{h}}{2})\right]\left[\phi_i(\underset{\sim}{\rho}-\frac{\underset{\sim}{h}}{2})+ibH\,\phi_s(\underset{\sim}{\rho}-\frac{\underset{\sim}{h}}{2})\right]$$
$$\times\, e^{\frac{-ie\underset{\sim}{H}\cdot[\underset{\sim}{h}\times\underset{\sim}{g}]}{2\hbar c}}\, U(\underset{\sim}{\rho}+\frac{\underset{\sim}{h}}{2})\left[1-\frac{ie\,\underset{\sim}{H}\cdot[\underset{\sim}{\rho}\times\underset{\sim}{h}]}{2\hbar c}\right] d\rho$$
$$= e^{-ie\frac{\underset{\sim}{H}\cdot[\underset{\sim}{h}\times\underset{\sim}{g}]}{2\hbar c}}\left[\int\left[\phi_i(\underset{\sim}{\rho}+\frac{\underset{\sim}{h}}{2})\,\phi_i(\underset{\sim}{\rho}-\frac{\underset{\sim}{h}}{2})+ibH\left[\phi_i(\underset{\sim}{\rho}+\frac{\underset{\sim}{h}}{2})\,\phi_s(\underset{\sim}{\rho}-\frac{\underset{\sim}{h}}{2})-\phi_s(\underset{\sim}{\rho}+\frac{\underset{\sim}{h}}{2})\,\phi_i(\underset{\sim}{\rho}-\frac{\underset{\sim}{h}}{2})\right.\right.\right.$$
$$\left.\left.\left.\times\, U(\underset{\sim}{\rho}+\frac{\underset{\sim}{h}}{2})\left[1-\frac{ie\,\underset{\sim}{H}\cdot[\underset{\sim}{\rho}\times\underset{\sim}{h}]}{2\hbar c}\right]\right] d^3\rho\right. \tag{3.3-12}$$

*Similar arguments can be made for tetrahedral sites as well.

or

$$J_{g,g+h} = e^{-ie\frac{H\cdot[h\times g]}{2hc}}\left[\int \phi_1(\underline{\rho}+\frac{\underline{h}}{2})\,\phi_1(\underline{\rho}-\frac{\underline{h}}{2})\,U(\underline{\rho}+\frac{\underline{h}}{2})\left[1-\frac{ie\,\underline{H}\cdot[\underline{h}\times\underline{\rho}]}{2hc}\right]d\right.$$

$$+ e^{-ie\frac{\underline{H}\cdot[\underline{h}\times\underline{g}]}{2hc}}\left[\int ibH\left[\phi_1(\underline{\rho}+\frac{\underline{h}}{2})\phi_s(\underline{\rho}-\frac{\underline{h}}{2})-\phi_s(\underline{\rho}+\frac{\underline{h}}{2})\phi_1(\underline{\rho}-\frac{\underline{h}}{2})\right]U(\underline{\rho}+\frac{\underline{h}}{2})\right.$$

(3.3-13)

It is noted that since 3d-waves have even parity the product wave function $\phi_1(\underline{\rho}+\frac{\underline{h}}{2})\,\phi_1(\underline{\rho}-\frac{\underline{h}}{2})$ is an even function while the term $[\phi_1(\underline{\rho}+\frac{\underline{h}}{2})\,\phi_s(\underline{\rho}-\frac{\underline{h}}{2})-\phi_s(\underline{\rho}+\frac{\underline{h}}{2})\,\phi_1(\underline{\rho}-\frac{\underline{h}}{2})]$ is an odd one. And assuming $U(r)$ has at least cylindrical symmetry one can show that (3.3-13) reduces to

$$J_{g,g+h} = e^{-ie\frac{\underline{H}\cdot[\underline{h}\times\underline{g}]}{2hc}}\int \phi_1(\underline{\rho}+\frac{\underline{h}}{2})\,\phi_1(\underline{\rho}-\frac{\underline{h}}{2})\,U(\underline{\rho}+\frac{\underline{h}}{2})\,d^3\rho\,, \qquad (3.3-14)$$

and defining

$$-J = \int \phi_1(\underline{\rho}+\frac{\underline{h}}{2})\,\phi_1(\underline{\rho}-\frac{\underline{h}}{2})\,U(\underline{\rho}+\frac{\underline{h}}{2})\,d^3\rho$$

$$= \int \phi_1(r)\,U(r)\,\phi_1(r-\underline{h})\,dV\,, \qquad (3.3-15)$$

we can write (3.3-14) as follows:

$$J_{g,g+h} = -J\,e^{i\alpha_{g,g+h}}\,. \qquad (3.3-16)$$

If we compare (3.3-16) with (3.8) we see that for 3d-waves the transfer integral between the wave functions of identical sites has got the same form as the Σ-states.

b) Assume that $\underline{g}$ and $g'=\underline{g}+\underline{h}$ are octahedral and tetrahedral sites respectively.

Substitution of (3.3-8) and (3.3-9) into (3.3-10) gives

$$J_{q,q+h} = \int \left[\phi_1(\underline{r}-\underline{q}) + ibH\phi_s \right]^* \left[\phi_s(\underline{r}-\underline{q}-\underline{h}) - ibH\,\phi_1(\underline{r}-\underline{q}-\underline{h}) \right]$$

$$\times U(\underline{r}-\underline{q})\; e^{-ie\frac{[H\times h]\cdot r}{2\hbar c}}\; dV \quad . \tag{3.3-17}$$

Transforming the integration variable to $\underline{\rho} = \underline{r}-\underline{q}-\frac{\underline{h}}{2}$ and expanding the exponent about $\underline{\rho}=0$ to terms linear in H, one has

$$J_{q,q+h} = e^{-ie\frac{\underline{H}\cdot[\underline{h}\times\underline{q}]}{2\hbar c}} \int \left[\phi_1(\underline{\rho}+\tfrac{\underline{h}}{2}) - ibH\,\phi_s(\underline{\rho}+\tfrac{\underline{h}}{2}) \right]$$

$$\times \left[\phi_s(\underline{\rho}-\tfrac{\underline{h}}{2}) - ibH\,\phi_1(\underline{\rho}-\tfrac{\underline{h}}{2}) \right] U(\underline{\rho}+\tfrac{\underline{h}}{2}) \left[1 - \frac{ie\underline{H}\cdot[\underline{h}\times\underline{\rho}]}{2\hbar c} \right] d^3\underline{\rho}$$

$$= e^{-\frac{ie\underline{H}\cdot[\underline{h}\times\underline{q}]}{2\hbar c}} \left\{ \int \phi_1(\underline{\rho}+\tfrac{\underline{h}}{2})\,\phi_s(\underline{\rho}-\tfrac{\underline{h}}{2})\,U(\underline{\rho}+\tfrac{\underline{h}}{2}) \left[1 - \frac{ie\underline{H}\cdot[\underline{h}\times\underline{\rho}]}{2\hbar c} \right] d^3\underline{\rho} \right.$$

$$- ibH \int \left[\phi_1(\underline{\rho}+\tfrac{\underline{h}}{2})\,\phi_1(\underline{\rho}-\tfrac{\underline{h}}{2}) + \phi_s(\underline{\rho}+\tfrac{\underline{h}}{2})\,\phi_s(\underline{\rho}-\tfrac{\underline{h}}{2}) \right] U(\underline{\rho}+\tfrac{\underline{h}}{2})$$

$$\left. \times \left[1 - \frac{ie\underline{H}\cdot[\underline{h}\times\underline{\rho}]}{2\hbar c} \right] d^3\underline{\rho} \right\}$$

(3.3-18)

or

$$J_{q,q+h} = e^{-\frac{ie\underline{H}\cdot(\underline{h}\times\underline{q})}{2\hbar c}}\left[\int \phi_1(\underline{\rho}+\frac{\underline{h}}{2})\,\phi_s(\underline{\rho}-\frac{\underline{h}}{2})\left[1-\frac{ie\underline{H}\cdot[\underline{h}\times\underline{\rho}]}{2\hbar c}\right]U(\underline{\rho}+\frac{\underline{h}}{2})\right.$$

$$= e^{-\frac{ie\underline{H}\cdot(\underline{h}\times\underline{q})}{2\hbar c}}\left[\int\left[\phi_1(\underline{\rho}+\frac{\underline{h}}{2})\phi_1(\underline{\rho}-\frac{\underline{h}}{2})+\phi_s(\underline{\rho}+\frac{\underline{h}}{2})\phi_s(\underline{\rho}-\frac{\underline{h}}{2})\right]U(\underline{\rho}+\frac{\underline{h}}{2})\right.$$

$$= e^{-\frac{ie\underline{H}\cdot(\underline{h}\times\underline{q})}{2\hbar c}}\left[-J - i\int\phi_1(\underline{\rho})\,\phi_s(\underline{\rho}-\underline{h})\,\frac{e\underline{H}\cdot[\underline{h}\times\underline{\rho}]}{2\hbar c}U(\underline{\rho})\,d\underline{\rho}\right.$$

$$-ibH\int\left[\phi_1(\underline{\rho})\,\phi_1(\underline{\rho}-\underline{h})+\phi_s(\underline{\rho})\,\phi_s(\underline{\rho}-\underline{h})\right]U(\underline{\rho})\,d\underline{\rho}\Big]$$

$$= -J\,e^{i\alpha_{q,q+h}}\left[1+\frac{i}{J}\int\phi_1(\underline{\rho})\,\phi_s(\underline{\rho}-\underline{h})\,\frac{e\underline{H}\cdot[\underline{\rho}\times\underline{h}]}{2\hbar c}U(\underline{\rho})\,d\underline{\rho}\right.$$

$$\left.+\frac{iHq}{J}\int\left[\phi_1(\underline{\rho})\,\phi_1(\underline{\rho}-\underline{h})+\phi_s(\underline{\rho})\,\phi_s(\underline{\rho}-\underline{h})\right]U(\underline{\rho})\,d\underline{\rho}\right]. \tag{3.3-19}$$

Then,

$$J_{q,q+h} \approx -J\,e^{i\alpha'_{q,q+h}}, \tag{3.3-20}$$

where

$$\alpha'_{q,q+h} = \alpha_{q,q+h} + \frac{1}{J}\int\phi_1(\underline{\rho})\,\phi_s(\underline{\rho}-\underline{h})\,\frac{e\underline{H}\cdot[\underline{\rho}\times\underline{h}]}{2\hbar c}U(\underline{\rho})\,d\underline{\rho}$$

$$+\frac{Hq}{J}\int\left[\phi_1(\underline{\rho})\,\phi_1(\underline{\rho}-\underline{h})+\phi_s(\underline{\rho})\,\phi_s(\underline{\rho}-\underline{h})\right]U(\underline{\rho})\,d\underline{\rho}. \tag{3.3-21}$$

From (3.3-20) we can say that for 3d-waves the transfer integral between the wave functions of non-identical sites is slightly different

from the corresponding transfer integral for Σ_- states. In this case we can define the flux relationship as

$$\alpha'_{q_3 q_2} + \alpha'_{q_2 q_1} + \alpha'_{q_1 q_3} = \frac{-e}{\hbar c} \underset{\sim}{H} \cdot \underset{\sim}{A}'_{321} . \qquad (3.3\text{-}22)$$

It may be remarked that, as in reference 19, it is not essential that the quantity A'_{321} be equal precisely to the area of the triangle defined by the sites $\underset{\sim}{q}_1$, $\underset{\sim}{q}_2$, and $\underset{\sim}{q}_3$.

APPENDIX 3A

Evaluation of the magnetic field-dependent contribution to the probability of occupation of site $\underset{\sim}{g}_3$:

As was discussed in reference (19), since we shall ultimately take the thermal average of (3.2-11) over all vibrational trajectories, we take advantage of the fact that for every vibrational trajectory $X_1(t), X_2(t), \ldots, X_q(t), \ldots, X_N(t)$, there are also corresponding time reversed trajectories $X_1(-t), X_2(-t), \ldots, X_q(-t), \ldots, X_N(-t)$ and therefore symmetrize the expression (3.2-12) with respect to time reversal and write

$$W_3^{(H)}\left(\tfrac{\pi}{2}\right) = \frac{1}{2}\left[W_3^{(H)}\left(\tfrac{\pi}{2}\right) + W_3^{(H)}\left(\tfrac{\pi}{2}\right)(\text{time reversed}) \right] . \quad (3A.1)$$

Substituting $W_3^{(H)}\left(\tfrac{\pi}{2}\right)$ and $W_3^{(H)}\left(\tfrac{\pi}{2}\right)(\text{time reversed})$ from (3.2-12) into (3A.1) and noting that

$$\phi_q(t)(\text{time reversed}) = \frac{A}{\hbar}\int_0^t X_q(-t')\,dt' = -\frac{A}{\hbar}\int_0^{-t} X_q(-t)\,dt' = -\phi_q(-t) \ ,$$

one finds (3A.1)

$$W_3^{(H)}\left(\tfrac{\pi}{2}\right) = \frac{\alpha J^3}{2\hbar^3}\left[\left(\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} dt' e^{-i[\phi_1(t') - \phi_3(t')]}\right)\left(\int_{\frac{\pi}{2}}^{\frac{\pi}{2}} dt' e^{i[\phi_2(t') - \phi_3(t')]}\int_{-\frac{\pi}{2}}^{t'} dt'' e^{i[\phi_1(t'') - \phi_2(t'')]}\right)\right.$$

$$\left. + \left(\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} dt' e^{i[\phi_1(-t') - \phi_3(-t')]}\right)\left(\int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} dt' e^{-i[\phi_2(-t') - \phi_3(-t')]}\int_{-\frac{\pi}{2}}^{t'} dt'' e^{-i[\phi_1(-t'') - \phi_2(-t'')]}\right)\right] + \text{C.C.} \quad (3A.3)$$

To proceed further, we change the variables of integrations in the time-reversed term to their negatives, i.e., $t' \longrightarrow -t'$, $t'' \longrightarrow -t''$; we then obtain

$$W_3^{(H)}\left(\frac{T}{2}\right) = \frac{\alpha J^3}{2\hbar^3}\left[\left(\int_{-\frac{T}{2}}^{\frac{T}{2}} dt' e^{-i[\phi_1(t')-\phi_3(t')]}\right)\left(\int_{-\frac{T}{2}}^{\frac{T}{2}} dt' e^{i[\phi_2(t')-\phi_3(t')]}\right)\left(\int_{-\frac{T}{2}}^{t'} dt'' e^{i[\phi_1(t'')-\phi_2(t'')]}\right)\right.$$

$$\left. + \left(\int_{-\frac{T}{2}}^{\frac{T}{2}} dt' e^{i[\phi_1(t')-\phi_3(t')]}\right)\left(\int_{-\frac{T}{2}}^{\frac{T}{2}} dt' e^{-i[\phi_2(t')-\phi_3(t')]}\right)\left(\int_{t'}^{\frac{T}{2}} dt'' e^{-i[\phi_1(t'')-\phi_2(t'')]}\right) + c.c.\right]. \tag{3A.4}$$

Since both terms in equation (3A.4) are real (because $W_3^{(H)}$ is real) we can easily replace the second term with its complex conjugate; then equation (3A.4) becomes

$$W_3^{(H)}\left(\frac{T}{2}\right) = \frac{\alpha J^3}{2\hbar^3}\left[\left(\int_{-\frac{T}{2}}^{\frac{T}{2}} dt' e^{-i[\phi_1(t')-\phi_3(t')]}\right)\left(\int_{-\frac{T}{2}}^{\frac{T}{2}} dt' e^{i[\phi_2(t')-\phi_3(t')]}\right)\left(\int_{-\frac{T}{2}}^{\frac{T}{2}} dt' e^{i[\phi_1(t')-\phi_2(t')]}\right)\right]. \tag{3A.5}$$

As discussed in reference (17), the present classical treatment is based on the fact that over the region of interest the following inequalities:

$$kT \gg \hbar\omega_0 \quad , \quad A^2/M\omega_0^2 > \hbar\omega_0, \tag{3A.6}$$

obtain, and the oscillations in the exponential integrands interfere destructively except at points of coincidence of the electronic energies (at which $X_1 = X_3$; $X_2 = X_3$ and $X_1 = X_3$). At such points, the phases of the above exponentials are momentarily stationary.

Further, as discussed in reference (19), we assume that at $t = t_{31} = 0$ within the interval $-\frac{T}{2}$ to $\frac{T}{2}$, one such point of stationary phase occurs between site $\underset{\sim}{g}_1$ and $\underset{\sim}{g}_3$. In addition, a coincidence of site $\underset{\sim}{g}_1$ and $\underset{\sim}{g}_2$ takes place at $t = t_{21}$ within the interval $-\frac{T}{2}$ to $\frac{T}{2}$. We also assume that in the neighbourhood of t_{31} and t_{12} the time variations of $X_3 - X_1$ and $X_1 - X_2$ may be taken to be linear. Denoting the relative velocity between sites i and j by

$$v_{ij} = v_i - v_j \,, \tag{3A.7}$$

one may write

$$x_1 - x_2 = v_{12}\,(t - t_{12}) \,, \tag{3A.8}$$

$$x_3 - x_1 = v_{31}\,t \,. \tag{3A.9}$$

Substituting (3A.8) and (3A.9) into (3A.5), one obtains

$$W_3^{(H)}\left(\frac{T}{2}\right) = \frac{\alpha J^3}{2\hbar^3} \exp\left(\frac{iA}{2\hbar} v_{12}\,\frac{v_{31}}{v_{23}}\,t_{12}^2\right) \int_{-\frac{T}{2}}^{\frac{T}{2}} dt \exp\left[\frac{iA}{2\hbar} v_{12}\,(t - t_{12})^2\right]$$

$$\int_{-\frac{T}{2}}^{\frac{T}{2}} dt' \exp\left[\frac{iA}{2\hbar} v_{23}\,(t' - t_{23})^2\right] \int_{-\frac{T}{2}}^{\frac{T}{2}} dt' \exp\left(\frac{iA}{2\hbar} v_{31}\,t'^2\right) + \text{c.c.} \tag{3A.10}$$

Now it is noticed that the important contributions to the individual integrals come from intervals

$$\Delta t \sim \left(\frac{\hbar}{A\,v_{ij}}\right)^{1/2} \sim \left[\frac{\hbar}{A\,(kT/M)^{1/2}}\right]^{1/2} = \frac{1}{\omega_0}\left[\frac{\hbar\omega_0}{(A^2/M\omega_0^3)^{1/2}(kT)^{1/2}}\right]^{1/2} \ll T \,.$$

Since we assume that $t_{13} = 0$ and $-\frac{T}{2} \leq t_{12} \leq \frac{T}{2}$ the individual limits of integration can be extended from $-\infty$ to ∞, and hence (3A.10) becomes

$$W_3^{(H)} = \frac{\alpha J^3}{2\hbar^3} \exp\left(\frac{iA}{2\hbar} v_{12}\,\frac{v_{31}}{v_{23}}\,t_{12}^2\right) \left[\left(\frac{2\pi\hbar}{A\,|v_{12}|}\right)^{1/2} e^{\pm i\frac{\pi}{4}}\right]$$

$$\times \left[\left(\frac{2\pi\hbar}{A\,|v_{23}|}\right)^{1/2} e^{\pm i\frac{\pi}{4}}\right]\left[\left(\frac{2\pi\hbar}{A\,|v_{31}|}\right)^{1/2} e^{\pm i\frac{\pi}{4}}\right] + \text{c.c.}, \tag{3A.11}$$

where $(\pm)$ in each bracket is taken according to whether $v_{ij} \gtrless 0$.

The result (3A.11) represents the transition probability for the previously described triple coincidence event.

APPENDIX 3B

Electric field modified occurrence-probability for the three-site coincidence event in the presence of induced electric dipoles:

To demonstrate the electric field modification of the occurrence probability, we first partly evaluate it in the absence of the external electric field. To do so we ignore the vibrational dispersion in the probability expression. According to the definition (3.2-16) this quantity is given by

$$P_T^c(v_{31}, v_{12}, t_{12})\,dt_{31}\,dt_{12}\,dv_{31}\,dv_{12} = \bar{Z}^{-1}\int\cdots\int dx_1\cdots dx_N\,dv_1\cdots dv_N \exp\left[-\frac{H_L+H_{int}}{kT}\right]$$
$$\times\,\delta\left[x_3(0)-x_1(0)\right]|v_{31}|\,dt_{31}\,\delta\left[v_3(0)-v_1(0)-v_{31}\right]\,dv_{31}$$
$$\times\,\delta\left[x_2(t_{12})-x_1(t_{12})\right]|v_{12}|\,dt_{12}\,\delta\left[v_2(t_{12})-v_1(t_{12})-v_{12}\right]dv_{12}\,, \tag{3B.1}$$

where

$$Z = \int\cdots\int dx_1\cdots dx_N\,dv_1\cdots dv_N \exp\left[-\frac{H_L+H_{int}}{kT}\right] \tag{3B.2}$$

is the vibrational partition function and

$$H_L + H_{int} = \sum_{\underset{\sim}{g}}\left(\frac{1}{2M}\,p_g^2 + \frac{1}{2}M\omega_0^2\,x_g^2\right) - Ax_1\,. \tag{3B.3}$$

Since we ignore the effect of the vibrational dispersion on the probability expression, the only pertinent integrations are those over the variables x_1, x_2, x_3, v_1, v_2 and v_3. Then considering only the relevant portion of H_L

$$H_L = \frac{1}{2}M\left(v_1^2+v_2^2+v_3^2\right) + \frac{1}{2}M\omega_0^2\left(x_1^2+x_2^2+x_3^2\right)\,, \tag{3B.4}$$

(3B.1) can be written in the following form:

$$P_T^c(v_{31}, v_{12}, t_{12})\, dt_{31}\, dt_{12}\, dv_{31}\, dv_{12} = I \times \frac{\iiint dx_1\, dx_2\, dx_3 \exp-\left[\frac{1}{2}M\omega_0^2(x_1^2+x_2^2+x_3^2) - Ax_1\right]/kT\ \delta(x_1-x_2)\,\delta(x_1-x_3)}{\iiint dx_1\, dx_2\, dx_3 \exp-\left[\frac{1}{2}M\omega_0^2(x_1^2+x_2^2+x_3^2) - Ax_1\right]/kT}, \tag{3B.5}$$

where

$$I = \frac{\iiint dv_1\, dv_2\, dv_3 \exp-\left[\frac{M}{2}(v_1^2+v_2^2+v_3^2)/kT\right] |v_{31}|\, dt_{31}\, \delta\left[v_3(0) - v_1(0) - v_{31}\right] dv_{31}\, |v_{12}|\, dt_{12}\, \delta\left[v_2(t_{12}) - v_1(t_{12}) - v_{12}\right] dv_{12}}{\iiint dv_1\, dv_2\, dv_3 \exp\left[-\frac{M}{2}(v_1^2+v_2^2+v_3^2)/kT\right]} \tag{3B.6}$$

Carrying out the integrations over the δ-functions, (3B.5) becomes

$$P_T^c(v_{31}, v_{12}, t_{12})\, dt_{31}\, dt_{12}\, dv_{31}\, dv_{12} = I \times \frac{e^{\frac{3}{2}\beta M\omega_0^2\left(\frac{x_0}{3}\right)^2} \int_{-\infty}^{\infty} dx_1\, e^{-\frac{3}{2}\beta M\omega_0^2\left(x_1 - x_0/3\right)^2}}{e^{\frac{\beta}{2}M\omega_0^2 x_0^2} \int_{-\infty}^{\infty} dx_1\, e^{-\frac{1}{2}\beta M\omega_0^2(x_1-x_0)^2} \int_{-\infty}^{\infty} dx_2\, e^{-\frac{\beta}{2}M\omega_0^2 x_2^2} \int_{-\infty}^{\infty} dx_3\, e^{-\frac{\beta}{2}M\omega_0^2 x_3^2}}, \tag{3B.7}$$

where $\beta = \frac{1}{kT}$ and $x_0 = \frac{A}{M\omega_0^2}$.

Introducing $\mathcal{E}_3 = \frac{1}{3}\frac{A^2}{M\omega_0^2}$ (3B.7) becomes

$$P_T^c(v_{31}, v_{12}, t_{12}) = I\ \frac{4}{3}\beta M\omega_0^2\ e^{-\beta\mathcal{E}_3}. \tag{3B.8}$$

To calculate the field modification of P_T^c in (3B.5), we replace $\delta(x_i - x_j)$ by $\delta\left(x_i - x_j - \frac{\Delta_{ji}}{A}\right)$ with

$$\Delta_{ji} = e E_0 \cdot h_{ji} + \left(W_{q_i}^p - W_{q_j}^p\right), \tag{3B.9}$$

where

$$h_{ji} = q_i - q_j . \tag{3B.10}$$

So the modified jump probability takes the form

$$P_T^c(E, v_{31}, v_{12}, t_{12})\, dt_{31}\, dt_{12}\, dv_{31}\, dv_{12} =$$

$$I \times \frac{\iiint dx_1 dx_2 dx_3 \exp\left[-\frac{M}{2}\omega_0^2(x_1^2+x_2^2+x_3^2)+Ax_1\right]/kT\ \delta\left(x_1-x_2-\frac{\Delta_{21}}{A}\right)\delta\left(x_1-x_3-\frac{\Delta_{31}}{A}\right)}{\iiint dx_1 dx_2 dx_3 \exp-\left[\frac{M}{2}\omega_0^2(x_1^2+x_2^2+x_3^2) - Ax_1\right]/kT} \tag{3B.11}$$

Carrying out the integrations over the δ-functions (3B.11) becomes

$$P_T^c(E, v_{31}, v_{12}, t_{12})\, dt_{31}\, dt_{12}\, dv_{31}\, dv_{12} = e^{(\Delta_{31}+\Delta_{21})/3kT}\ I\ \frac{4}{3}\beta M\omega_0^2\, e^{-\beta E_3} . \tag{3B.12}$$

Comparing (3B.12) with (3B.8) we see that

$$P_T^c(E, v_{31}, v_{12}, t_{12}) = e^{(\Delta_{31}+\Delta_{21})/3kT}\ P_T^c(v_{31}, v_{12}, t_{12}) . \tag{3B.13}$$

Substitution of Δ_{31} and Δ_{21} from (3B.9) and (3B.10) gives the electric field modified jump rate for a polarizable dielectric:

$$P_T^c(E, v_{31}, v_{12}, t_{12}) = e^{\frac{1}{3kT}\left[eE_0(q_3-q_2)+(W_{q_1}^p-W_{q_3}^p)+eE_0(q_3-q_2)+(W_{q_1}^p-W_{q_2}^p)\right]}\ P_T^c(v_{31}, v_{12}, t_{12}) \tag{3B.14}$$

CHAPTER IV

A.C. IMPURITY HOPPING CONDUCTION

4.1 Introduction and review of experiments on ac impurity hopping conduction:

Having considered the local field corrections to small polaron dc hopping conductivity, we proceed with the ac impurity hopping conductivity.

The first observation of a frequency dependent conductivity $\sigma(\omega)$ for a compensated n-type silicon in the impurity hopping conduction range were reported by Pollak and Geballe[33]. The frequency dependence could be expressed by the empirical relation

$$\sigma(\omega) = \sigma - \sigma_{dc} = A\omega^{S}. \qquad (4.1)$$

Here, ω is the radian frequency and takes values between 10^2 and 10^5 cps. The exponent S was found to have a value close to 0.8, and A is complex. The measurements were carried out at temperatures between 1 and 20°K. At low temperatures, the conductivity is roughly proportional to minority impurity concentration and is almost independent of the majority impurity concentration, while at higher temperatures the conductivity becomes approximately proportional to the product of both concentrations. The theory of this phenomenon is dominated by the pair approximation which was first introduced by Pollak and Geballe[33] and later extended by Pollak in several papers[39,40]. The model which they considered for ac conductivity is based on the Mott-Conwell model[41,42] for the dc impurity conduction. According to that model, in a semiconductor containing N_d donor and N_a acceptor states with energies ε_d and ε_a such that $E_v < \varepsilon_a < \varepsilon_d < E_c$, ($E_v$ and E_c being the upper valence and the lower conduction band edges respectively) a fraction $K = N_A/N_D \ll 1$ of the donor

states will be compensated allowing for finite transition probabilities of the carriers between occupied and vacant impurity sites. One then expects impurity conduction at low temperatures; $kT < E_c - E_d$. Due to compensation, acceptor states become ionized and thus produce local varying Coulomb fields which remove the degeneracy of the donor states and leads to a statistical distribution of the donor energies with a mean energy difference Δ between neighbouring sites. According to the Anderson localization principle[36], impurity hopping conduction occurs when the ratio Δ / I (I being the mean overlap) is larger than a critical value. Since I is exponentially decreasing with the mean distance between the donor states, one expects impurity hopping conduction for low concentration. The donor concentrations below which this model is appropriate is about 2×10^{17} in n-type silicon.

With such a model, an applied ac field causes Debye type dielectric losses, because of the presence of the polarization current which is due to unequivalency of the impurity sites[43].

The particular theory of the ac impurity conduction which we concentrate on is the pair approximation of Pollak and Geballe[33]. As far as the local field problem is concerned, the pair approximation will be adequate for investigation of the local field concentration to ac hopping conductivity.

4.2 AC hopping conduction in the pair approximation:

For weak compensation, one may divide the volume of the crystal into cells, each centred around a charged minority impurity. Each cell contains a carrier which hops among the majority centres, with the centre closest to the minority centre having the highest probability of carrier occupation. Further, one may assume that the carrier motion in each cell is unaffected by the motion of the carriers in other cells. The latter assumption enables us to consider the current as an additive function of the contribution from all cells*. In the pair approximation, one assumes that hopping in each cell occurs predominantly between pairs of majority impurities.

Now consider the conductivity of a cube of 1 cm^3 with N identical jumping centres. Assume that each centre consists of a pair of majority impurity atoms separated by an energy ΔE, distance r, and having all the same orientation θ with respect to the applied field $\underset{\sim}{E}_0$. Letting the indices $1, 2$ represent two atoms of the n pairs, we can write the conductivity as

$$J = \hat{P} \quad , \tag{4.2}$$

where

$$\rho = -ne\left(x_1 f_1 + x_2 f_2\right) \quad ; \tag{4.3}$$

here $(-e)$ is the electronic charge, x_1 and x_2 are the projections along the field direction of the separation of the two atoms of each of the pairs; f_1 and f_2 are the occupation probabilities of site 1 and 2 in each pair respectively, and related to each other by the normalization condition

$$f_1 + f_2 = 1 \quad . \tag{4.4}$$

*This assumption is experimentally justified by the almost linear dependence of σ on minority impurity concentration.

Then f_1 (or f_2) is determined by the rate equation :

$$\dot{f}_1 = W_{12} f_2 - W_{21} f_1 = -(W_{21} + W_{12}) f_1 + W_{12} \,, \qquad (4.5)$$

where W_{ij} is the transition rate[26] from site j to i and is given by

$$W_{ji} \propto \frac{\Delta E/2kT}{\sinh(\Delta E/2kT)} \exp\left(-2\alpha R - \Delta E/2kT\right) \qquad (4.6)$$

for $E_j < E_i$, and

$$W_{ji} \propto \frac{\Delta E/2kT}{\sinh(\Delta E/2kT)} \exp\left(-2\alpha R + \Delta E/2kT\right) \qquad (4.7)$$

for $E_j > E_i$.

Here $\Delta E = |E_i - E_j|$, where E_i and E_j are the energies of the electron at site i and j respectively, R is the distance between two sites, and $\exp(-2\alpha R)$ is the overlap term resulting from the spherical symmetrical wave function of the centres which fall of as $\exp(-\alpha r)$. Then the current becomes

$$J = \dot{P} = -ne(x_1 - x_2)\dot{f}_1 = -ner\cos\theta\,\dot{f}_1 \,. \qquad (4.8)$$

In the absence of the applied field, $\dot{f}_1$ vanishes and no current flows, as expected. Then the system will be in thermal equilibrium and we have the condition of detailed balancing:

$$\frac{W_{12}^{\circ}}{W_{21}^{\circ}} = \exp\left\{(E_1 - E_2)/kT\right\} = \exp\left(-\Delta E/kT\right) \,, \qquad (4.9)$$

where $\Delta E = |\varepsilon_1 - \varepsilon_2|$ and we assume that $\varepsilon_1 < \varepsilon_2$.
Then equation (4.5) has the uniform thermal equilibrium solution

$$f_1(0) = \frac{\exp(-\Delta E/kT)}{1 + \exp(-\Delta E/kT)} \quad . \tag{4.10}$$

To find the current, one must solve the differential equation (4.5) in the presence of the applied field, $\mathcal{E}$. We assume that the electric field is a step function of time:

$$\mathcal{E} = 0 \qquad \text{for} \quad t \leq 0$$
$$\mathcal{E} = E_0 \qquad \text{for} \quad t > 0 \ .$$

In the presence of the field the transition rates are altered, favouring sites of low field energy and a current will flow. The transition rates, W_{12} and W_{21}, in the presence of the field, also satisfy the detailed balancing condition with

$$\Delta E = |\varepsilon_1 - \varepsilon_2 + e\underset{\sim}{E}_0 \cdot (\underset{\sim}{q}_1 - \underset{\sim}{q}_2)| = |\varepsilon_1 - \varepsilon_2 + eE_0 r\cos\theta|$$

($\underset{\sim}{q}_1$ and $\underset{\sim}{q}_2$ being the vectors going to atoms 1 and 2 respectively):

$$\frac{W_{12}}{W_{21}} = \exp \frac{|(\varepsilon_1 - \varepsilon_2) + eE_0 r\cos\theta|}{kT} \ . \tag{4.11}$$

Then the solution of (4.5) has the following form:

$$f_1 = \frac{W_{12}}{W_{12} + W_{21}} + C\exp(-Kt) \ , \tag{4.12}$$

where $K = \tau^{-1} = W_{12} + W_{21}$. The coefficient C is determined from the boundary condition

$$C = f_1(0) - f_1(\infty) \tag{4.13}$$

with

$$f_1(0) = \frac{W_{12}^{\circ}}{W_{12}^{\circ} + W_{21}^{\circ}} \quad , \tag{4.14}$$

$$f_1(\infty) = \frac{W_{12}}{W_{12} + W_{21}} \quad . \tag{4.15}$$

By virtue of (4.13), (4.14) and (4.15) the solution (4.12) can be written as

$$f_1(t) = f_1(\infty) + \left[f_1(0) - f_1(\infty) \right] \exp(-Kt) \tag{4.16}$$

or

$$f_1(t) = \frac{W_{12}}{W_{12} + W_{21}} + \left[\frac{W_{12}^{\circ}}{W_{12}^{\circ} + W_{21}^{\circ}} - \frac{W_{12}}{W_{12} + W_{21}} \right] \exp(-Kt) \quad . \tag{4.17}$$

To calculate the current we make use of the symmetry properties of the problem and rewrite (4.8) in the following form:

$$J = -\frac{1}{2} n e r \cos\theta \, (\dot{f}_1 - \dot{f}_2) \quad . \tag{4.18}$$

From (4.16) $\dot{f}_1(t)$ can be calculated :

$$\dot{f}_1(t) = -K \left[f_1(0) - f_1(\infty) \right] \exp(-Kt)$$

$$= -K \left[\frac{W_{12}^{\circ}}{W_{12}^{\circ} + W_{21}^{\circ}} - \frac{W_{12}}{W_{12} + W_{21}} \right] \exp(-Kt) \quad . \tag{4.19}$$

With a similar argument we can write

$$\dot{f}_2(t) = -K \left[f_2(0) - f_2(\infty) \right] \exp(-Kt)$$

$$= -K \left[\frac{W_{21}^{\circ}}{W_{12}^{\circ} + W_{21}^{\circ}} - \frac{W_{21}}{W_{12} + W_{21}} \right] \exp(-Kt) \quad , \tag{4.20}$$

where $$f_2(0) = \frac{W_{21}^0}{W_{12}^0 + W_{21}^0}$$

and $$f_2(\infty) = \frac{W_{21}}{W_{12} + W_{21}} . \qquad (4.21)$$

Substituting (4.20) and (4.19) into (4.18) we get :

$$J = \frac{1}{2} n e r \cos\theta K \left[\frac{W_{12}^0}{W_{12}^0 + W_{21}^0} - \frac{W_{21}^0}{W_{12}^0 + W_{21}^0} - \frac{W_{12}}{W_{12} + W_{21}} + \frac{W_{21}}{W_{12} + W_{21}} \right] \exp(-Kt) . \qquad (4.22)$$

In the pair approximation the field is assumed to be small; hence (4.11) is approximated by :

$$\frac{W_{12}}{W_{21}} = \frac{W_{12}^0}{W_{21}^0} \left(1 + \frac{e E_0 r \cos\theta}{kT} \right) = \exp\left(-\frac{\Delta E}{kT} \right) \left(1 + \frac{e E_0 r \cos\theta}{kT} \right) . \qquad (4.23)$$

Substituting (4.23) into (4.22), we get:

$$J = \frac{1}{4} n e r \cos\theta \, \tau^{-1} \frac{1}{\cosh^2(\Delta E / 2kT)} \frac{e E_0 r \cos\theta}{kT} \exp(-t/\tau) . \qquad (4.24)$$

Transforming (4.24) into the frequency-dependent form:

$$\frac{J(\omega)}{E_0(\omega)} = \frac{1}{4} n e^2 r^2 \cos\theta \frac{1}{kT \cosh^2(\Delta E / 2kT)} \tau^{-1} \left[\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} + i \frac{\omega \tau}{1 + \omega^2 \tau^2} \right] . \qquad (4.25)$$

To consider the contribution from all the pairs in each cell, equation (4.25) must be integrated over ΔE, r and θ:

$$d\sigma(r, \theta, \Delta E, \omega) = \frac{1}{4} d\rho(r, \theta, \Delta E) N_A e^2 r^2 \cos^2\theta \frac{1}{kT \cosh^2(\Delta E / 2kT)} \times \tau^{-1} \left[\frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad \frac{i \omega \tau}{1 + \omega^2 \tau^2} \right] , \qquad (4.26)$$

where $dP(r,\theta,\Delta E)$ is the number of pairs of spacing r, orientation θ, and energy separation ΔE ; N_A is the total density of pairs and is equal to the number of acceptors.

When ΔE is not much larger than kT , $\cosh^2(\Delta E/2kT)$ is close to unity, and hence at high enough temperature we can probably neglect the ΔE dependence. And assuming that the impurities are randomly distributed, we can write :

$$dP(r,\theta,\Delta E) = 2\pi N_D r^2 \sin\theta \, dr \, d\theta . \tag{4.27}$$

Substituting (4.27) into (4.26) and integrating over θ , $Re(\sigma)$ becomes :

$$Re\left[\sigma'(\omega)\right] = \frac{1}{12} N_A N_D \frac{e^2}{kT} \int_0^\infty r^2 \tau^{-1} \frac{(\omega\tau)^2}{1+(\omega\tau)^2} 4\pi r^2 dr . \tag{4.28}$$

The integral (4.28) is calculated by Pollak and Geballe[33]. The result is

$$Re\left[\sigma'(\omega)\right] = \frac{4\pi}{12} N_D N_A \frac{e^2}{kT} \left(14.8 - \frac{1}{2}\ln\omega\right)^4 (a^2/2) \times \omega \left\{ \frac{\pi}{2} - \arctan\left[5.5 \times 10^{-13} \omega \left(14.8 - \tfrac{1}{2}\ln\omega\right)^{3/2} \tan(\Delta E/2kT) \right] \right\} . \tag{4.29}$$

It is noticed that[33] for frequencies below 10^7 , $Re\left[\sigma'(\omega)\right]$ can be expressed as

$$Re\left[\sigma'(\omega)\right] \propto N_A N_D \omega^{0.8} , \tag{4.30}$$

which is in good agreement with the experimental results.

4.3 Investigation of the local field correction to ac impurity hopping conduction:

In the presence of the applied field, as a result of the formation of induced dipoles the energy difference, ΔE , and hence transition rates and occupation probabilities are modified. The energy difference is augmented to include the interaction of the electron with the induced dipoles

$$\Delta E \longrightarrow \left| (\varepsilon_1 - \varepsilon_2) + e\,\underset{\sim}{E}_0 \cdot (\underset{\sim}{q}_1 - \underset{\sim}{q}_2) + (W^p_{q_1} - W^p_{q_2}) \right| \qquad (4.31)$$

where $W^p_{q_1}$ and $W^p_{q_2}$ are the dipolar energies at sites 1 and 2 respectively. So from (4.31), it is seen that the possibility for local field correction arises due to the presence of the extra term $(W^p_{q_1} - W^p_{q_2})$. As was seen in chapter II, the investigation of the local field correction problem reduces to an evaluation of $(W^p_{q_1} - W^p_{q_2})$ for neighbouring donor sites. In the presence of the applied field two mechanisms contribute to the total polarization. Namely, electronic contribution from the polarizable atoms and polarization due to charged donor-acceptor pairs. However for small compensation the concentration of such pairs is small and the latter contribution can be neglected. For arbitrary compensation this is not so and this case will be considered at some future time.

Then, $W^p_{\underset{\sim}{q}}$ can be written as

$$W^p_{\underset{\sim}{q}} = -e \sum_{\underset{\sim}{q}' \neq \underset{\sim}{q}} \frac{\underset{\sim}{p}_{\underset{\sim}{q}'} \cdot (\underset{\sim}{q} - \underset{\sim}{q}')}{|\underset{\sim}{q} - \underset{\sim}{q}'|^3} \,, \qquad (4.32)$$

where $\underset{\sim}{p}_{\underset{\sim}{q}}$ is the induced dipole at site $\underset{\sim}{q}$. Normally $\underset{\sim}{p}_{\underset{\sim}{q}}$ can take the values p_0 , p_A and p_c , the dipole moment of a donor, an acceptor and the host ion respectively. Now assuming that

$$\underset{\sim}{p}_0 \simeq \underset{\sim}{p}_A \simeq \underset{\sim}{p}_c \,,$$

we can set $\underset{\sim}{\rho}_{\underset{\sim}{q}} = \underset{\sim}{\rho}$ in (4.32). Then $W^{\rho}_{\underset{\sim}{q}_1}$ and $W^{\rho}_{\underset{\sim}{q}_2}$ become

$$W^{\rho}_{\underset{\sim}{q}_1} = -e \sum_{\underset{\sim}{q}' \neq \underset{\sim}{q}_1} \frac{\underset{\sim}{\rho} \cdot (\underset{\sim}{q}_1 - \underset{\sim}{q}')}{|\underset{\sim}{q}_1 - \underset{\sim}{q}'|^3} \quad , \tag{4.33}$$

$$W^{\rho}_{\underset{\sim}{q}_2} = -e \sum_{\underset{\sim}{q}' \neq \underset{\sim}{q}_2} \frac{\underset{\sim}{\rho} \cdot (\underset{\sim}{q}_2 - \underset{\sim}{q}')}{|\underset{\sim}{q}_2 - \underset{\sim}{q}'|^3} \quad , \tag{4.34}$$

To evaluate $(W^{\rho}_{\underset{\sim}{q}_1} - W^{\rho}_{\underset{\sim}{q}_2})$ we calculate $W^{\rho}_{\underset{\sim}{q}_1}$ and $W^{\rho}_{\underset{\sim}{q}_2}$ independently. The reason for this is that in this case $\underset{\sim}{q}_1$ and $\underset{\sim}{q}_2$ are not necessarily neighbouring sites, therefore the argument made in section (2.4) does not seem to be straighforward. However following Appendix 2G, $W^{\rho}_{\underset{\sim}{q}_1}$ and $W^{\rho}_{\underset{\sim}{q}_2}$ can be written as

$$W^{\rho}_{\underset{\sim}{q}_1} = e\, \underset{\sim}{E}_1 \cdot (\underset{\sim}{q}_1 - \underset{\sim}{q}_0) \quad , \tag{4.35}$$

$$W^{\rho}_{\underset{\sim}{q}_2} = e\, \underset{\sim}{E}_1 \cdot (\underset{\sim}{q}_2 - \underset{\sim}{q}_0) \quad , \tag{4.36}$$

where $\underset{\sim}{q}_0$ is the vector going to the centre of mass.

From (4.35) and (4.36) $(W^{\rho}_{\underset{\sim}{q}_1} - W^{\rho}_{\underset{\sim}{q}_2})$ becomes

$$W^{\rho}_{\underset{\sim}{q}_1} - W^{\rho}_{\underset{\sim}{q}_2} = e\, \underset{\sim}{E}_1 \cdot (\underset{\sim}{q}_1 - \underset{\sim}{q}_2) \quad . \tag{4.37}$$

Substitution of (4.37) into (4.31) gives

$$\Delta E \rightarrow \left| (\epsilon_1 - \epsilon_2) + e\, \underset{\sim}{E}_{mac} \cdot (\underset{\sim}{q}_1 - \underset{\sim}{q}_2) \right| \tag{4.38}$$

From equation (4.38) we conclude that the net electric field appearing in the transition rates and occupation probabilities is just the macroscopic electric field, $\underset{\sim}{E}_{mac}$. Therefore we do not expect local field type corrections to ac impurity hopping conductivity.

CHAPTER V

QUANTUM THEORY OF ELECTRIC TRANSPORT IN THE PRESENCE OF INDUCED DIPOLES

5.1 Introduction:

Having investigated local field type corrections to small polaron hopping and impurity hopping conduction, it is now our task to extend these results to the band motion of electrons and to find a more general result for the electrical conductivity. The problem of electrical conductivity is usually treated on the basis of a transport equation[29]. This is an equation for the distribution function $f = f(k, r, t)$ which describes how electrons are distributed in (k, r) space at any time, t. The transport equation says that in the steady state the time rate of change of the distribution function must vanish, that is :

$$\left(\frac{\partial f}{\partial t}\right) = 0 \quad . \tag{5.1}$$

In the absence of temperature gradients and magnetic fields, two essentially distinct factors contribute to change of the distribution function with time; namely, acceleration of electrons by an external electric field and collision of electrons with imperfections in the crystal lattice. Therefore (5.1) is written as the sum of two contributions:

$$\left(\frac{\partial f}{\partial t}\right)_{Field} + \left(\frac{\partial f}{\partial t}\right)_{collision} = 0 \quad . \tag{5.2}$$

Jones and Zener[30] examined the action of uniform electric field on the motion of an electron in a crystal lattice using quantum mechanics and concluded that the field term in equation (5.2) could

be written as

$$\left(\frac{\partial f}{\partial t}\right)_{Field} = e\,\underset{\sim}{E}_0 \cdot \underset{\sim}{\nabla}_k f(\underset{\sim}{k},\underset{\sim}{r}) , \tag{5.3}$$

where e is the magnitude of the charge of the electron, $\underset{\sim}{E}_0$ is the applied electric field (units are chosen such that $\hbar = 1$).

The collision term in (5.2) may be described in general by scattering processes which take an electron from an initial state $\underset{\sim}{k}$ to a final state $\underset{\sim}{k}'$. If $W(\underset{\sim}{k}',\underset{\sim}{k})$ denotes the probability per unit time that an electron in the state $\underset{\sim}{k}$ makes a transition to state $\underset{\sim}{k}'$ due to collisions, the change in the distribution function from these processes is

$$\left(\frac{\partial f}{\partial t}\right)_{collision} = \frac{1}{(2\pi)^3}\int\left\{f(\underset{\sim}{k}')\left[1-f(\underset{\sim}{k})\right]W(\underset{\sim}{k},\underset{\sim}{k}') - f(\underset{\sim}{k})\left[1-f(\underset{\sim}{k}')\right]W(\underset{\sim}{k}',\underset{\sim}{k})\right\} d^3\underset{\sim}{k}'\, d^3\underset{\sim}{r} . \tag{5.4}$$

The scatterings by static imperfections are usually assumed to be elastic, i.e.,

$$\mathcal{E}(\underset{\sim}{k}) = \mathcal{E}(\underset{\sim}{k}') . \tag{5.5}$$

In this case the detailed balancing condition ,

$$\frac{W(\underset{\sim}{k},\underset{\sim}{k}')}{W(\underset{\sim}{k}',\underset{\sim}{k})} = e^{\left[\mathcal{E}(\underset{\sim}{k}) - \mathcal{E}(\underset{\sim}{k}')\right]/kT} ,$$

results in

$$W(\underset{\sim}{k},\underset{\sim}{k}') = W(\underset{\sim}{k}',\underset{\sim}{k}) . \tag{5.6}$$

So, for elastic scatterings (5.4) reduces to

$$\left(\frac{\partial f}{\partial t}\right)_{\text{collision}} = \frac{1}{(2\pi)^3}\int \left[f(\underset{\sim}{k}') - f(\underset{\sim}{k})\right] W(\underset{\sim}{k},\underset{\sim}{k}')\, d^3\underset{\sim}{k}'\, d^3\underset{\sim}{r} \quad . \tag{5.7}$$

Inserting (5.3) and (5.7) into (5.2), we obtain the Boltzmann transport equation, if only elastic collisions are considered:

$$0 = e\,\underset{\sim}{E}_0 \cdot \nabla_k f(\underset{\sim}{k},\underset{\sim}{r}) + \frac{1}{(2\pi)^3}\int \left[f(\underset{\sim}{k}') - f(\underset{\sim}{k})\right] W(\underset{\sim}{k},\underset{\sim}{k}')\, d^3\underset{\sim}{k}\, d^3\underset{\sim}{r} \quad . \tag{5.8}$$

Once equation (5.8) has been solved for $f(\underset{\sim}{k},\underset{\sim}{r})$, all of the various transport properties of a conductor can be calculated.

Equation (5.2) itself is incomplete in several respects. First it is well known that a quantum mechanical calculation of the average of a physical quantity requires in general not only the probabilities of the different state being occupied, but the entire density matrix. Now the occupation probabilities of some complete set of states are just the diagonal elements of the density matrix in this representation. Therefore a theory of transport based on quantum mechanical principles is required. Kohn and Luttinger[12] provided such a theory on the basis of a simple model which gives the entire density matrix of a system of charge carriers in the steady state. Their model consisted of non-interacting free (or Bloch) electrons being scattered by randomly located rigid impurity centres. The density matrix was developed in ascending powers of the strength of the scattering potential. They showed that the familiar Boltzmann transport equation represents an approximation valid in the limiting cases of very weak scattering.

5.2 Mathematical Formalism:

In the present work, we develop a quantum theory of electrical transport in the presence of induced dipoles in the system, within the framework already set up by Kohn and Luttinger[12]. For the sake of simplicity, we do not include the effects of a magnetic field. (The magnetic field effects in the absence of induced dipoles have been considered in detail by Thomas[32]). We consider a collection of electrons so dilute that their interaction with each other and the effect of Fermi-Dirac statistics on their behaviour can be neglected. Then every electron may be treated as completely independent of all the others and one has essentially a single electron problem. The electrons are treated as free (or being in a periodic potential) except for their interaction with a scattering potential, the externally applied electric field, and the potential due to induced dipoles in the crystal.

The total Hamiltonian, H_T, for each electron moving in such a system may be written as

$$H_T = H_0 + H' + H_F + H_D \,, \tag{5.9}$$

where the first three terms have already been defined by Kohn and Luttinger. Namely, H_0 is the Hamiltonian of the free (or Bloch) electrons, H' is the interaction with the impurity centres, and H_F is the interaction with the external electric field. The last term, H_D, is the interaction with the induced dipoles and is the additional contribution of the present work. The various terms of (5.9) are given by

$$H_0 = \frac{p_\alpha^2}{2m} \,, \quad \text{for free electrons} \,, \tag{5.10}$$

$$H_0 = \frac{p_\alpha^2}{2m} + U \,, \quad \text{for Bloch electrons} \,, \tag{5.11}$$

$$H' = \sum_{i=1}^{N} \phi(\underset{\sim}{r} - \underset{\sim}{r}_i) = \lambda V \,, \tag{5.12}$$

$$H_F = e E_\alpha X_\alpha \,, \tag{5.13}$$

and

$$H_D = -e \sum_{\underset{\sim}{g}} \frac{\underset{\sim}{p}_{\underset{\sim}{g}} \cdot (\underset{\sim}{r} - \underset{\sim}{g})}{|\underset{\sim}{r} - \underset{\sim}{g}|^3} \,, \tag{5.14}$$

where $p_\alpha = -i \frac{\partial}{\partial x_\alpha}$ is the free particle momentum operator. Here it is understood that α is to be summed from one to three. In (5.12), λ is some dimensionless measure of the strength of the interaction of the impurity with the electron, $\phi(r)$ is the interaction with a single impurity centre and $\underset{\sim}{r}_i$ are the locations of the N impurity centres. In (5.13) and (5.14), e is the magnitude of the charge of the electron, $\underset{\sim}{E}_0$ is the externally applied electric field, and $\underset{\sim}{p}_{\underset{\sim}{g}}$ is the induced dipole moment at each lattice site $\underset{\sim}{g}$ and is assumed to be proportional to and parallel to the applied field and identical for all sites $\underset{\sim}{g}$.

We may write

$$H = H_0 + H' \,, \tag{5.15}$$

the total Hamiltonian in the absence of the external field.

Consider a collection of ν electrons moving under the action of the total Hamiltonian, H_T and introduce the exact density matrix ρ_T for this collection. Denote the time-dependent wave functions of the electrons by $\Psi^i(\underset{\sim}{r}, t)$ and expand them in a complete set of time-independent functions $\phi_m(\underset{\sim}{r})$:

$$\Psi(r,t) = \sum_m a_m^i(t)\,\phi_m(r) \quad . \tag{5.16}$$

The Hermitian matrix $\rho_T(\rho, r, t)$ with the elements

$$(\rho_T)_{mm'} = \frac{1}{N}\sum_{i=1}^{N} a_m^i(t)\; a_{m'}^{i*}(t) \tag{5.17}$$

in the ϕ_m representation, is the exact density matrix[31]. The expectation value of any observable quantity represented by the operator $M(t)$ is then given by

$$\overline{M(t)} = Tr\left\{\rho_T(t)\,M(t)\right\} \quad , \tag{5.18}$$

where Tr means the trace or diagonal sum of the corresponding matrix. The time variation of $\rho_T(t)$ is given by

$$i\frac{\partial \rho_T}{\partial t} = \left[H_T, \rho_T\right] \quad , \tag{5.19}$$

(again the units are chosen such that $\hbar = 1$.)

The diagonal elements $[\rho_T]_{mm}$ give the probability of finding an electron in the state $\phi_m(r)$. The sum of all these probabilities is of course unity for a wave function normalized to unity. If ρ_T can be found from (5.19), the observed value of any operator quantity (for example the conductivity) can be found by means of equation (5.18).

In the absence of an electric field, the system will exist in a state of equilibrium. The exact equilibrium density matrix ρ must then satisfy the equation

$$i\frac{\partial \rho}{\partial t} = \left[H, \rho\right] = \left[H_0 + H', \rho\right] \quad . \tag{5.20}$$

It is known from the theory of statistical mechanics that the exact form of the function must be a canonical distribution at temperature T :

$$\rho = K e^{-\beta H} = K e^{-\beta [H_0 + H']} . \qquad (5.21)$$

Here $\beta = \frac{1}{kT}$, where k is the Boltzmann constant and T is the absolute temperature. $H_0 + H'$ must be used in (5.21) (instead of simply H_0), since at equilibrium the electrons are not free but are interacting with the scattering potential H' . The normalization constant K must be determined from the trace

$$K^{-1} = Tr\{ e^{-\beta H} \} \qquad (5.22)$$

and will depend on both H_0 and H' .

5.3 The Boltzmann Transport Equation:

Imagine that in the very remote past $(t=-\infty)$ a collection of electrons existed in equilibrium with a heat bath at temperature T under the influence of a set of N randomly distributed impurities. There is no external field present. Then at $t=-\infty$ contact with the heat bath is broken and the electric field is very slowly turned on adiabatically according to

$$E_\alpha = E_{0\alpha}\, e^{st} \quad , \quad -\infty < t \leq 0 \; , \tag{5.23}$$

so that the electric field is zero at $t=-\infty$ and reaches its full value, $E_{0\alpha}$, at time zero. It will be seen that the results do not depend on the frequency parameter s as long as it is chosen reasonably. The collection of electrons is now described by the single-particle density matrix, ρ_T, whose time development is given by (5.19). The solution of interest will be that for $t=0$, when the electric field reaches its full value $E_{0\alpha}$.

To calculate the total density matrix, ρ_T, we expand it in powers of E_α. Therefore in general we will have

$$\rho_T = \rho + \rho_F + \rho_2 + \cdots \; , \tag{5.24}$$

where ρ_F is linear in E_α, ρ_2 is quadratic and so on. Inserting (5.24) into (5.19) and equating equal powers of E_α, we obtain the following equations:

$$i\frac{\partial \rho}{\partial t} = [H, \rho] \quad , \text{ zero'th order in } E_\alpha \; ,$$

$$i\frac{\partial \rho_F}{\partial t} = [H, \rho_F] + [H_F + H_0, \rho] \quad , \text{ first order in } E_\alpha \; ,$$

$$i\frac{\partial \rho_2}{\partial t} = [H, \rho_2] + [H_F + H_0, \rho_F] \quad , \text{ second order in } E_\alpha \, ,$$

$$i\frac{\partial \rho_n}{\partial t} = [H, \rho_n] + [H_F + H_0, \rho_{n-1}] \quad , \text{ nth order in } E_\alpha \, ,$$

and so on.

It is noted that these equations can be solved by an iterative procedure. Here we shall limit ourselves to the linear equation, namely, to the evaluation of ρ_F (ohmic region), the higher order terms being left to Appendix 5E:

$$i\frac{\partial \rho_F}{\partial t} = [H_F + H_0, \rho] + [H, \rho_F] \, . \tag{5.25}$$

The quantity ρ_F must satisfy the initial condition

$$\rho_F\,(t=-\infty) = 0 \, . \tag{5.26}$$

Now H_F and H_0 may be written as

$$H_F = H_E\, e^{st} \quad , \quad H_E = e\, E_{0\alpha}\, X_\alpha \, , \tag{5.27}$$

$$H_0 = H_P\, e^{st} \quad ; \quad H_P = -e\sum_{\underline{g}} \frac{P_{\underline{g}}\cdot(\underline{r}-\underline{g})}{(\underline{r}-\underline{g})} \, , \tag{5.28}$$

Equations (5.25) and (5.26) can be satisfied with the Ansatz

$$\rho_F = f\, e^{st} \, , \tag{5.29}$$

where f is linear in the electric field and independent of time.

Inserting (5.27), (5.28) and (5.29) into (5.25) we get

$$is\,f = [H_E, \rho] + [H_P, \rho] + [H, f] \quad . \tag{5.30}$$

Here we note that H_P is treated like H_E rather than like H'. The reason is that it is an induced effect and proportional to the applied field.

To solve equation (5.30), which is valid for any representation, we chose the representation for which H_o is diagonal. These are plane waves with periodic boundary conditions for free electrons and Bloch waves for Bloch electrons. In the following we give the solutions for free electrons to the lowest order effects in λ, the strength of the interaction of the electrons with the impurities. Later we generalize the discussion to the case of Bloch electrons.

a) Free electron case:

The normalized eigenfunctions are

$$|\underset{\sim}{k}\rangle = \phi_{\underset{\sim}{k}} = \frac{e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}}}{\Omega^{1/2}} \quad , \tag{5.31}$$

where Ω is the volume of the specimen.

In Dirac notation we can write

$$H_o\,|\underset{\sim}{k}\rangle = \mathcal{E}^o_{\underset{\sim}{k}}\,|\underset{\sim}{k}\rangle \quad , \tag{5.32}$$

where

$$\mathcal{E}^o_{\underset{\sim}{k}} = \frac{\underset{\sim}{k}^2}{2m} \quad . \tag{5.33}$$

In this representation, (5.30) becomes

$$(\omega_{\underset{\sim}{k}\underset{\sim}{k}'} - is)\, f_{\underset{\sim}{k}\underset{\sim}{k}'} = C_{\underset{\sim}{k}\underset{\sim}{k}'} + D_{\underset{\sim}{k}\underset{\sim}{k}'} + \sum_{\underset{\sim}{k}''} \left(f_{\underset{\sim}{k}\underset{\sim}{k}''} H'_{\underset{\sim}{k}''\underset{\sim}{k}'} - H'_{\underset{\sim}{k}\underset{\sim}{k}''} f_{\underset{\sim}{k}''\underset{\sim}{k}'} \right) \quad , \tag{5.34}$$

where $\omega_{kk'} = \varepsilon^0_k - \varepsilon^0_{k'}$, $C = [\rho, H_\varepsilon]$ and $D = [\rho, H_\phi]$.

The matrix elements of H' are easily obtained ;

$$H'_{kk'} = \langle \underline{k}| H' |\underline{k}'\rangle = \frac{1}{\Omega}\int_\Omega e^{-i(\underline{k}-\underline{k}')\cdot\underline{r}} \sum_{i=1}^{N} \phi(\underline{r}-\underline{r}_i)\, d^3\underline{r}$$

$$= \frac{1}{\Omega}\sum_i e^{-i(\underline{k}-\underline{k}')\cdot\underline{r}_i} \int_\Omega e^{-i(\underline{k}-\underline{k}')\cdot\underline{r}} \phi(\underline{r})\, d^3\underline{r}$$

$$= \frac{\phi_{kk'}}{\Omega}\sum_{i=1}^{N} e^{-i(\underline{k}-\underline{k}')\cdot\underline{r}_i} , \qquad (5.35)$$

where

$$\phi_{kk'} = \int e^{-i(\underline{k}-\underline{k}')\cdot\underline{r}} \phi(\underline{r})\, d^3\underline{r} . \qquad (5.36)$$

For simplicity, we assumed that $\phi(\underline{r})$ has a finite range so that the coordinate integration in (5.36) can be extended over all space. It is easily seen from (5.35) and (5.36) that the diagonal elements of H' are independent of $\underline{k}$ and just equal to the (spatial) average potential ϕ .

If we split (5.34) into diagonal and non-diagonal parts we may write ;

$$-is f_k = C_k + D_k + \sum_{k'(\neq k)} \left(f_{kk'} H'_{k'k} - H'_{kk'} f_{k'k} \right) , \qquad (5.37)$$

for $k = k'$, and

$$(\omega_{kk'} - is) f_{kk'} = C_{kk'} + D_{kk'} + (f_k - f_{k'}) H'_{kk'} + f_{kk'}(H'_{kk'} - H'_{kk})$$

$$+ \sum_{k''(\neq k, k')} \left(f_{kk''} H'_{k''k'} - H'_{kk''} f_{k''k'} \right) , \qquad (5.38)$$

for $\underset{\sim}{k} \neq \underset{\sim}{k}'$. Here $f_k = f_{kk}$, $C_k = C_{kk}$ and $D_k = D_{kk}$. Since the diagonal elements of H' are equal, the fourth term on the right-hand side of (5.38) vanishes. Then (5.38) becomes

$$(\omega_{kk'} - is) f_{kk'} = C_{kk'} + D_{kk'} + (f_k - f_{k'}) H'_{kk'} + \sum_{\underset{\sim}{k}'' (\neq \underset{\sim}{k}, \underset{\sim}{k}')} (f_{kk''} H'_{k''k'} - H'_{kk''} f_{k''k'}) . \quad (5.39)$$

We will solve equation (5.39) to lowest order in λ . To do this we investigate the λ dependence of the different terms for small λ .

We begin with the commutator ,

$$C_{kk'} = [\rho, H_E]_{kk'} = e E_0 \alpha [\rho (H_0 + H'), X_\alpha]_{kk'} . \quad (5.40)$$

Now we may expand ρ in powers of H' and this gives for $C_{kk'}$ a power series in λ . Therefore in general we have ,

$$C_{kk'} = C^{(0)}_{kk'} + C^{(1)}_{kk'} + C^{(2)}_{kk'} + \cdots , \quad (5.41)$$

$C^{(n)}_{kk'}$ being proportional to λ^n . We shall limit ourselves only to the calculation of $C^{(0)}_{kk'}$. In the lowest order

$$\rho = \rho_0 = K_0 e^{-\beta H_0} = K_0 \exp\left(-\beta \frac{p_\alpha^2}{2m}\right) . \quad (5.42)$$

Using the commutation rules (or $X_\alpha = i \frac{\partial}{\partial p_\alpha}$), we obtain the operator relationship .

$$C = e E_0 \alpha [\rho, X_\alpha] = e E_0 \alpha \frac{1}{i} \frac{\partial \rho}{\partial p_\alpha} . \quad (5.43)$$

From (5.43) and (5.42) we can write down $C^{(o)}_{kk'}$:

$$C^{(o)}_{kk'} = eE_0 \propto \frac{1}{i}\left(\frac{\partial \rho_0}{\partial p_\alpha}\right)_{kk} = -eE_0 \propto \frac{1}{i} K_0 \frac{\beta}{m} \left(p_\alpha e^{-\beta H_0}\right)_{kk'}$$

$$= -eE_0 \propto \frac{1}{i} K_0 \frac{\beta}{m} \sum_{k''} \langle k| p_\alpha |k''\rangle \langle k''| e^{-\beta H_0} |k'\rangle = -eE_0 \propto \frac{1}{i} K_0 \frac{\beta}{m} k_\alpha \delta_{kk'} e^{-\beta \varepsilon^0_{k'}} \delta_{kk'} . \tag{5.44}$$

Defining

$$\rho_k = K_0 e^{-\beta \varepsilon^0_k} , \tag{5.45}$$

we may write

$$C^{(o)}_{kk'} = -ie E_0 \propto \left(\frac{\partial \rho_k}{\partial k_\alpha}\right) \delta_{kk'} . \tag{5.46}$$

Here the derivative occurring in (5.46) is the formal derivative and (5.46) is meant to be identical with (5.44), the question of whether the allowed value of $\underset{\sim}{k}$ are discrete or continuous playing no role.

From (5.46) it is seen that $C^{(o)}_{kk'}$ has diagonal elements only. Thus the diagonal terms of C begin with zero'th order in λ while the off-diagonal ones are of the first order in λ .

The next quantity to consider is the commutator

$$D_{kk'} = [\rho, H_P]_{kk'} = -e\left[\rho, \sum_{\underset{\sim}{q}} \frac{\underset{\sim}{p_q} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3}\right]_{kk'} . \tag{5.47}$$

Similarly we can write

$$D_{kk'} = D^{(o)}_{kk'} + D^{(1)}_{kk'} + D^{(2)}_{kk'} + \cdots , \tag{5.48}$$

$D^{(n)}_{kk'}$ being proportional to λ^n . Here also we shall limit ourselves only to the calculation of $D^{(o)}_{kk'}$. In Appendix 5A we study this additional commutator which arises from the induced dipoles. We prove, by the method of induction, that $D^{(o)}_{kk'}$ has only diagonal elements and that they take the form

$$D^{(o)}_{kk} = -e\left[\rho_0, \sum_{\underset{\sim}{q}} \frac{\underset{\sim}{p_q} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3}\right]_{kk} = -e\left[\nabla_r \sum_{\underset{\sim}{q}} \frac{\underset{\sim}{p_q} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3}\right]_{kk} \cdot [\rho_0, \underset{\sim}{r}]_{kk} . \tag{5A.14}$$

On the other hand, in Appendix 5B we show that

$$\left[-\nabla_r \sum_{\underset{\sim}{q}} \frac{\underset{\sim}{p_q} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3}\right]_{kk} = \underset{\sim}{E}_1 , \tag{5B.7}$$

where E_1 is the depolarization field for free electrons.

Thus from (5A.14) and (5B.7) we can write that

$$D^{(0)}_{kk'} = e E_{1\alpha} [\rho_0, x_\alpha]_{kk'} = -i e E_{1\alpha} \frac{\partial f_k}{\partial k_\alpha} \delta_{kk'} \quad (5.49)$$

From (5.49) it is seen that the diagonal terms of D begin with zero'th order in λ while the off-diagonal ones are of the first order in λ. From the result of usual transport theory we can say that f_k is of order λ^{-2} (f_k is inversely proportional to the transition probabilities). If we assume this, then it follows at once from (5.39), (5.46) and (5.49) that $f_{kk'}$ $(k \neq k')$ is of order λ^{-1}. Thus (5.39) can be solved by an iterative procedure. From the orders in λ discussed above, we see at once that on the right-hand side of (5.39) the third term dominates and we obtain

$$f_{kk'} = \frac{(f_k - f_{k'}) H'_{kk'}}{(\omega_{kk'} - i s)} \quad (5.50)$$

in lowest order. If we insert this into (5.37) and retain only the lowest order terms in λ, we obtain

$$-is f_k = -ie E_{0\alpha} \frac{\partial f_k}{\partial k_\alpha} - ie E_{1\alpha} \frac{\partial f_k}{\partial k_\alpha} + \sum_{k' (\neq k)} |H'_{kk'}|^2 \left[(f_k - f_{k'}) \left(\frac{1}{\omega_{kk'} - is} - \frac{1}{\omega_{kk'} + is} \right) \right] \quad (5.51)$$

or

$$-is f_k = -ie E_{mac\alpha} \frac{\partial f_k}{\partial k_\alpha} + \sum_{k' (\neq k)} |H'_{kk'}|^2 \left[(f_k - f_{k'}) \left(\frac{1}{\omega_{kk'} - is} - \frac{1}{\omega_{kk'} + is} \right) \right], \quad (5.52)$$

where

$$\underset{\sim}{E}_{mac} = \underset{\sim}{E}_0 + \underset{\sim}{E}_1 \quad , \tag{5.53}$$

the macroscopic electric field.

It will now be shown that (5.52) is just the usual Boltzmann transport equation in the presence of induced dipoles. Inserting for $H'_{kk'}$ its value from (5.35) gives

$$|H'_{kk'}|^2 = \frac{|\phi_{kk'}|^2}{\Omega^2} \sum_{i,j} e^{-i(\underline{r}_i - \underline{r}_j)\cdot \underline{q}} \quad , \tag{5.54}$$

where $\underline{q} = \underline{k} - \underline{k}' \neq 0$. The quantity $|H'_{kk'}|^2$ depends in general on the position of all the impurities, namely for each arrangement of impurities it will have some definite value. Let us define the ensemble average of $|H'_{kk'}|^2$, say $\langle |H'_{kk'}|^2 \rangle$, as the average of $|H'_{kk'}|^2$ over all the different arrangements of the impurities, without any correlation between the impurities. That is :

$$\langle |H'_{kk'}|^2 \rangle = \int_{\Omega} \cdots \int_{\Omega} \frac{d\underline{r}_1}{\Omega} \frac{d\underline{r}_2}{\Omega} \cdots \frac{d\underline{r}_N}{\Omega} \, |H'_{kk'}|^2 \, . \tag{5.55}$$

The value of $|H'_{kk'}|^2$ will in general deviate from $\langle |H'_{kk'}| \rangle$, the deviation depending on the position of the impurities. However, if as $N \to \infty$ the fluctuations approach zero, we can regard $|H'_{kk'}|^2$ as a well defined quantity equal to its ensemble average for all but a negligible fraction of possible arrangements of impurities. But, direct calculation shows that for $|H'_{kk'}|^2$ this is not true and the fluctuations approach unity rather than zero.

$$\lim_{N\to\infty} \frac{\langle (|H'_{kk'}|^2)^2\rangle - \langle |H'_{kk'}|^2\rangle^2}{\langle |H'_{kk'}|^2\rangle^2} = \frac{(|\phi_{kk'}|^2/\Omega^2)^2 (2N^2+N-N^2)}{(|\phi_{kk'}|^2/\Omega^2) N^2} \to 1$$

Now consider the summation over k' in (5.52). Kohn and Luttinger show that since $\omega_{kk'}$ is a smooth function of k' as is $f_{kk'}$, the summation over k' in (5.32) may be broken up into regions of momentum space in which $\omega_{kk'}$ and $f_{kk'}$ do not vary appreciably, but $|H'_{kk'}|^2$ may. Let the number of states in such a region be ν. In general ν will be of the order N, i.e.,

$$\nu = \alpha N ,$$

where α is some very small number independent of N. Therefore if we consider instead of $|H'_{kk'}|^2$ the quantity

$$M = \frac{1}{\nu} \sum_{k' \text{ in } \nu} |H'_{kk'}|^2 ,$$

it is shown by Kohn and Luttinger that as $N \to \infty$ the fluctuations for M approach zero:

$$\lim_{N\to\infty} \frac{\langle M^2\rangle - \langle M\rangle^2}{\langle M\rangle^2} \to 0 .$$

Hence M is a well defined quantity equal to its ensemble average for all but a negligible fraction of possible arrangement of the impurities. Therefore without any loss of rigour we may replace $|H'_{kk'}|^2$ in (5.52) by its ensemble average

$$\langle |H'_{kk'}|^2\rangle = \frac{N}{\Omega} |\phi_{kk'}|^2 . \qquad (5.56)$$

Inserting this into (5.52) gives

$$-is f_k = -ie E_{mac} \frac{\partial \rho_k}{\partial k_\alpha} + \frac{N}{\Omega^2} \sum_{k'(\neq k)} |\phi_{kk'}|^2 (f_k - f_{k'}) \left(\frac{1}{\omega_{kk'} - is} - \frac{1}{\omega_{kk'} + is} \right) . \tag{5.57}$$

The solution of (5.57) depends in general on the value of the frequency parameter s. However, there is a very large range of s (including the physically interesting rates with which the field could be turned on) for which the solution is practically independent of s. This range corresponds to those values very much smaller than the characteristic frequencies of the problem:

$$s \ll t_r^{-1}, t_a^{-1},$$

where t_r is of the order of the collision relaxation time and t_a is an "atomic time". In the present problem t_a would be of the order of $\hbar / \mathcal{E}_a$ or $r_0 / \bar{v}$, where $\mathcal{E}_a$ is a typical energy of the electron, r_0 is the size of an impurity and $\bar{v}$ is a typical electron velocity. Further, if $s \gg \Delta E/\hbar$, (where ΔE is of the order of the spacing of the translational electronic energy levels) the sum in (5.57) may be replaced by an integral according to

$$\sum_{\underset{\sim}{k}'} \longrightarrow \frac{\Omega}{(2\pi)^3} \int d^3 \underset{\sim}{k}' . \tag{5.58}$$

Once this has been done, the condition $s \ll t_a^{-1}$ allows one to use the well known result

$$\lim_{s \to 0} \left(\frac{1}{x - is} \right) = P\left(\frac{1}{x}\right) + i\pi \delta(x) , \tag{5.59}$$

where $P\left(\frac{1}{x}\right)$ is the principal value of $\frac{1}{x}$ and $\delta(x)$

is the ordinary Dirac δ – function.

The condition $s \ll t_r^{-1}$ implies that as $s \to 0$, the term $s f_k$ on the left-hand side of (5.57) becomes very much smaller compared to the second term on the right-hand side (which is of the order of $t_r^{-1} f_k$) hence can be dropped. Therefore (5.57) becomes

$$0 = -e E_{mac} \alpha \frac{\partial f_k}{\partial k_\alpha} + \frac{2\pi N}{\Omega^2} \sum_{k'} |\phi_{kk'}|^2 \delta(\omega_{kk'}) (f_k - f_{k'}) . \tag{5.60}$$

Note that this equation is in lowest order in λ. Now the transition probability $\omega^{(0)}_{kk'}$ per unit time from a plane-wave state k' to k due to a single impurity may be written, in the lowest Born approximation, as

$$\omega^{(0)}_{kk'} = 2\pi \frac{|\phi_{kk'}|^2}{\Omega^2} \delta(\omega_{kk'}) \tag{5.61}$$

If we define the total transition probability $W^{(0)}_{kk'}$ as the sum of those occurring due to each of the impurities, then we have

$$0 = -e E_{mac} \alpha \frac{\partial f_k}{\partial k_\alpha} + \sum_{k'(\neq k)} \left(W^{(0)}_{kk'} f_k - W_{kk'} f_{k'} \right) , \tag{5.62}$$

which is the customary transport equation used in the theory of impurity conduction in the presence of induced dipoles in the system. The first term is the acceleration term due to the external electric field and the field of induced dipoles. The second term is just the rate of change of the distribution function due to collisions with the randomly distributed impurities.

Once (5.62) has been solved for the diagonal part of the density matrix, f_k, the off-diagonal elements can be obtained from (5.50) to lowest order in λ.

From Eq. (5.62) we conclude that the net electric field appearing in the transport equation is just the macroscopic field, E_{mac}.

b) Electrons in a periodic potential:

In this part, we generalize the results of the previous part to the case where the electrons are moving in a periodic potential as well as the external electric field and the field of induced dipoles and scattering centres. We shall take the same type of impurity potential as before but for simplicity assume that impurities are randomly distributed on lattice sites. The perturbation H' is the same as (5.12), the only difference being that $\phi(r)$ represents the difference between the potential produced by an impurity atom and that of the original atom of the periodic lattice.

In this case H_o is given by

$$H_o = \frac{p_\alpha^2}{2m} + U \quad , \tag{5.63}$$

where U is the periodic potential. We shall assume that the eigenfunctions and eigenvalues of (5.63) are known:

$$H_o \phi_\ell = \mathcal{E}_\ell^{(o)} \phi_\ell \quad , \tag{5.64}$$

$$\phi_\ell = |n,k\rangle = \frac{e^{ik\cdot r}}{\Omega^{1/2}} u_\ell(r) \quad , \tag{5.65}$$

where $u_\ell(r)$ is a function which has the periodicity of the lattice. Here the index ℓ stands for the index pair (n,k), n telling us the band and k being a wave vector whose allowed values extend over the first Brillouin zone. The ϕ_ℓ are assumed to be orthonormal:

$$\langle n',k' | n,k \rangle = \int \phi_{\ell'}^* \phi_\ell \, d^3r = \delta_{\ell\ell'} = \delta_{nn'} \delta_{kk'} \quad . \tag{5.66}$$

We shall use as our basic representation the representations in which H_0 is diagonal (ℓ representation) and carry out the calculations for the same band. In other words we assume that the perturbation is not strong enough or sharp enough to induce interband transitions. (For example Zener effect and optical transition to a higher band). In this representation (5.30) becomes

$$(\omega^{(0)}_{\ell\ell'} - is) f_{\ell\ell'} = C_{\ell\ell'} + D_{\ell\ell'} + \sum_{\ell''} (f_{\ell\ell''} H'_{\ell''\ell'} - H'_{\ell\ell''} f_{\ell''\ell'}), \tag{5.67}$$

which is formally identical with (5.34) except that k is replaced everywhere by ℓ .

In this case the matrix elements of H' are

$$H'_{\ell\ell'} = \int \phi_\ell^* H' \phi_{\ell'} \, d^3r$$

$$= \frac{\phi_{\ell\ell'}}{\Omega} \left[\sum_i e^{i(k-k')\cdot r_i} \right] , \tag{5.68}$$

where

$$\phi_{\ell\ell'} = \int_\Omega e^{-i(k-k')\cdot r} u_\ell^*(r) u_{\ell'}(r) \phi(r) \, d^3r . \tag{5.69}$$

In deriving this we have used the fact that the impurities are found at lattice points. Equation (5.68) has exactly the same form as (5.35) except that $\phi_{kk'}$ is replaced by $\phi_{\ell\ell'}$. The diagonal elements of H'' are

$$H'_{\ell\ell} = \left(\frac{N}{\Omega}\right) \phi_{\ell\ell} , \tag{5.70}$$

with

$$\phi_{\ell\ell} = \int |u_\ell|^2 \phi(r) \, d^3r . \tag{5.71}$$

From (5.70) and (5.71) it is noted that $H'_{\ell\ell}$ will be a definite function of ℓ .

Now the method of solution of (5.67) is identical with the free electron case, involving a split into diagonal and off-diagonal terms in ℓ . So the corresponding equations for (5.37) and (5.38) are

$$-is f_k = C_\ell + O_\ell + \sum_{\ell'(\neq\ell)} \left(f_{\ell\ell'} H'_{\ell'\ell} - H'_{\ell\ell'} f_{\ell'\ell} \right) , \tag{5.72}$$

for $\ell = \ell'$, and

$$(\omega^{(0)}_{\ell\ell'} - is) f_{\ell\ell'} = C_{\ell\ell'} + O_{\ell\ell'} + (f_\ell - f_{\ell'}) H'_{\ell\ell'}$$

$$+ f_{\ell\ell'} (H'_{\ell'\ell'} - H'_{\ell\ell}) + \sum_{\ell''(\neq\ell,\ell')} \left(f_{\ell\ell''} H'_{\ell''\ell'} - H'_{\ell\ell''} f_{\ell''\ell'} \right) , \tag{5.73}$$

for $\ell \neq \ell'$. Here $f_\ell = f_{\ell\ell}$, $C_\ell = C_{\ell\ell}$ and $O_\ell = O_{\ell\ell}$. Since the diagonal elements of H' are not equal, the fourth term on the right-hand side of (5.73) does not vanish as before. In this case we adopt the following convention: if $H'_{\ell\ell}$ depends on ℓ , we absorb this diagonal part of H' into H_0 and take as our unperturbed energy

$$\mathcal{E}_\ell = \mathcal{E}^0_\ell + H'_{\ell\ell} , \tag{5.74}$$

and defining $\omega_{\ell\ell'} = \mathcal{E}_\ell - \mathcal{E}_{\ell'}$, we rewrite (5.73) as

$$(\omega_{\ell\ell'} - is) f_{\ell\ell'} = C_{\ell\ell'} + O_{\ell\ell'} + (f_\ell - f_{\ell'}) H'_{\ell\ell'}$$

$$+ \sum_{\ell''(\neq\ell,\ell')} \left(f_{\ell\ell''} H'_{\ell''\ell'} - H'_{\ell\ell''} f_{\ell''\ell'} \right) . \tag{5.75}$$

Here also we will solve the equation (5.75) to the lowest order in λ .

We begin with the commutator

$$C_{ee'} = \left[\rho, H_E \right]_{ee'} = e E_0 \alpha \left[\rho (H_0 + H'), \chi_\alpha \right] . \tag{5.76}$$

Once again we may write

$$C_{ee'} = C_{ee'}^{(0)} + C_{ee'}^{(1)} + C_{ee'}^{(2)} + \cdots , \tag{5.77}$$

$C_{ee'}^{(n)}$ being proportional to λ^n . Again we limit ourselves only to the calculation of $C_{ee'}^{(0)}$. In the lowest order

$$\rho = \rho_0 = K_0 e^{-\beta H_0} = K_0 \exp\left[-\beta \left(\frac{P_\alpha^2}{2m} + U \right) \right] . \tag{5.78}$$

Using the commutation rules, we obtain the operator relationship

$$C = e E_0 \alpha \left[\rho, \chi_\alpha \right] = e E_0 \alpha \frac{1}{i} \frac{\partial \rho}{\partial P_\alpha} . \tag{5.79}$$

From (5.78) and (5.79) we can write down $C_{ee'}^{(0)}$:

$$C_{ee'}^{(0)} = e E_0 \alpha \frac{1}{i} \left(\frac{\partial \rho_0}{\partial P_\alpha} \right)_{ee'} = - e E_0 \alpha \frac{1}{i} K_0 \frac{\beta}{m} \left(P_\alpha e^{-\beta H_0} \right)_{ee'}$$

$$= - e E_0 \alpha \frac{1}{i} K_0 \frac{\beta}{m} \sum_{k''} \langle nk | P_\alpha | nk'' \rangle \langle nk'' | e^{-\beta H_0} | nk' \rangle$$

$$= - e E_0 \alpha \frac{1}{i} K_0 \frac{\beta}{m} e^{-\beta E_{nk'}} \langle nk | P_\alpha | nk' \rangle . \tag{5.80}$$

In Appendix 5C we demonstrate that the intra-band matrix elements of the momentum operator has only diagonal elements, namely,

$$\langle nk | P_\alpha | nk' \rangle = m \frac{\partial E_{nk}}{\partial k_\alpha} \delta_{kk'} . \tag{5.81}$$

Substitution of (5.81) into (5.80) gives

$$C^{(0)}_{\ell\ell'} = -e\,E_0\alpha\,\frac{1}{i}\,K_0\,\beta\,\frac{\partial \varepsilon_{nk}}{\partial k_\alpha}\,e^{-\beta\varepsilon_{nk}}\,\delta_{kk'} . \tag{5.82}$$

Defining

$$\rho_\ell = K_0\,e^{-\beta\varepsilon_{nk}} , \tag{5.83}$$

we may write

$$C^{(0)}_{\ell\ell'} = -i\,e\,E_0\alpha\left(\frac{\partial \rho_\ell}{\partial k_\alpha}\right)\delta_{kk'} . \tag{5.84}$$

From (5.84) it is seen that $C^{(0)}_{\ell\ell'}$ has diagonal elements only. Thus the diagonal terms of C begin with zero'th order in λ, while the off-diagonal ones are of the first order in λ. Next, we consider the commutator,

$$D_{\ell\ell'} = [\rho, H_\rho]_{\ell\ell'} = -e\left[\rho, \sum_{\underline{q}} \frac{\rho_{\underline{q}}\cdot(\underline{r}-\underline{q})}{|\underline{r}-\underline{q}|^3}\right]_{\ell\ell'} . \tag{5.85}$$

Similarly we can write

$$D_{\ell\ell'} = D^{(0)}_{\ell\ell'} + D^{(1)}_{\ell\ell'} + D^{(2)}_{\ell\ell'} + \cdots) \tag{5.86}$$

$D^{(n)}_{\ell\ell'}$ being proportional to λ^n. Here again we limit ourselves only to the calculation of $D^{(0)}_{\ell\ell}$. In Appendix 5A we show that also $D^{(0)}_{\ell\ell'}$ has diagonal elements only and they take the form

$$D^{(0)}_{\ell\ell'} = -i\,e\,E_1\alpha\,\frac{\partial \rho_\ell}{\partial k_\alpha}\,\delta_{kk'} . \tag{5.87}$$

Thus the diagonal terms of D begin with zero'th order in λ while the off-diagonal ones are of first order in λ .

Since in zero'th order the off-diagonal elements of C and D are zero, to proceed further we follow exactly the same arguments as in the free electron case. Therefore everything leading to (5.62) may be repeated in the ℓ representation. This gives rise to an equation which is formally identical with (5.62) except that $\underset{\sim}{k}$ is replaced everywhere by ℓ . Since all the algebra is identical we shall only state the result:

$$0 = -e E_{mac} \frac{\partial f_\ell}{\partial k_\alpha} + \sum_{\ell' (\neq \ell)} \left(W^{(0)}_{\ell' \ell} f_\ell - W^{(0)}_{\ell \ell'} f_{\ell'} \right) , \qquad (5.88)$$

where the quantity $W^{(0)}_{\ell' \ell}$ is again the total transition probability of an electron going from state ℓ to ℓ' .

From (5.88) we conclude that, even for Bloch electrons, the net electric field appearing in the transport equation is just the macroscopic electric field, $\underset{\sim}{E}_{mac}$, not the local electric field.

Appendix 5A: Proof of the relations:

$$D^{(o)}_{kk'} = -ie\,E_{1\alpha}\,\frac{\partial \rho_k}{\partial k_\alpha}\,\delta_{kk'} \tag{5A.1}$$

and

$$D^{(o)}_{ee'} = -ie\,E_{1\alpha}\,\frac{\partial \rho_e}{\partial k_\alpha}\,\delta_{kk'}\,. \tag{5A.2}$$

To zero'th order, the diagonal elements of D, in the k representation, are

$$D^{(o)}_{kk'} = \left[\rho_o, H_p\right]_{kk} = -e\left[\rho_o, \sum_{\underline{g}} \frac{\rho_g\cdot(\underline{r}-\underline{g})}{|\underline{r}-\underline{g}|^3}\right]_{kk}. \tag{5A.3}$$

First we shall prove that for a general function $f(\underline{r})$ we have the following relation:

$$\left[\rho_o, f(\underline{r})\right]_{kk} = \left[\nabla f(\underline{r})\right]_{kk}\cdot\left[\rho_o, \underline{r}\right]_{kk} \tag{5A.4}$$

or

$$\left[\rho_o, f(\underline{r})\right]_{kk} = \left(\frac{\partial f}{\partial x_\alpha}\right)_{kk}\left[\rho_o, x_\alpha\right]_{kk} = -i\left(\frac{\partial f}{\partial x_\alpha}\right)_{kk}\left(\frac{\partial \rho_o}{\partial p_\alpha}\right)_{kk}. \tag{5A.5}$$

Here we have used that $\left[\rho_o, x_\alpha\right] = -i\,\frac{\partial \rho_o}{\partial p_\alpha}$, and it is understood that α must be summed from one to three. To prove (5A.5) we shall expand $\rho_o(\underline{\rho})$ in Maclaurin series and use the induction method:

$$\rho_o(\underline{\rho}) = \rho(\underline{\rho}=0) + \rho_\alpha\,\rho_{\rho_\alpha}(\underline{\rho}=0) + \frac{\rho_\alpha\,\rho_\beta}{2!}\,\rho_{\rho_\alpha\rho_\beta}(\underline{\rho}=0) + \cdots, \tag{5A.6}$$

where

$$\rho_{p_\alpha} = \frac{\partial \rho_0}{\partial p_\alpha} \tag{5A.7}$$

and

$$\rho_{p_\alpha p_\beta} = \frac{\partial^2 \rho_0}{\partial p_\alpha \partial p_\beta} \quad , \tag{5A.8}$$

where it is understood that α and β must be summed from one to three.

To proceed further, for a general term (for example n^{th} term) we must show that

$$\left[p_\alpha^n , f(\xi) \right]_{kk} = -i \left(\frac{\partial f}{\partial x_\alpha} \right)_{kk} \left(\frac{\partial p_\alpha^n}{\partial p_\alpha} \right)_{kk} = -i n \left(\frac{\partial f}{\partial x_\alpha} \right)_{kk} \left(p_\alpha^{n-1} \right)_{kk} . \tag{5A.9}$$

Now for $n=1$ (5A.9) becomes

$$\left[p_\alpha , f(\xi) \right]_{kk} = -i \left(\frac{\partial f}{\partial x_\alpha} \right)_{kk} , \tag{5A.10}$$

which is a well-known result in Quantum Mechanics. Then (5A.9) is true for $n=1$.

We assume that (5A.9) is true for any n and prove that it is also true for $(n+1)$, i.e.

$$\left[p_\alpha^{n+1} , f(\xi) \right]_{kk} \stackrel{?}{=} -i (n+1) \left(\frac{\partial f}{\partial x_\alpha} \right)_{kk} \left(p_\alpha^n \right)_{kk} . \tag{5A.11}$$

The left-hand side of (5A.11) can be written as

$$\left[P_\alpha^{n+1}, f(\underline{r}) \right]_{kk} = \left\{ P_\alpha^{n+1} f(\underline{r}) - f(\underline{r}) P_\alpha^{n+1} \right\}_{kk}$$

$$\equiv \left[P_\alpha P_\alpha^n f(\underline{r}) - P_\alpha f(\underline{r}) P_\alpha^n + P_\alpha f(\underline{r}) P_\alpha^n - f(\underline{r}) P_\alpha^{n+1} \right]_{kk}$$

$$= \left\{ P_\alpha \left[P_\alpha^n, f(\underline{r}) \right] + \left[P_\alpha, f(\underline{r}) \right] P_\alpha^n \right\}_{kk}$$

$$= (P_\alpha)_{kk} \left[P_\alpha^n, f(\underline{r}) \right]_{kk} + \left[P_\alpha, f(\underline{r}) \right]_{kk} (P_\alpha^n)_{kk} \, . \tag{5A.12}$$

Here we have used that P_α and P_α^n are diagonal in the k representation. Now substituting the value of $\left[P_\alpha^n, f(\underline{r}) \right]_{kk}$ and $\left[P_\alpha, f(\underline{r}) \right]_{kk}$ from (5A.9) and (5A.10) into the right-hand side of (5A.12), we get

$$\left[P_\alpha^{n+1}, f(\underline{r}) \right]_{kk} = (P_\alpha)_{kk} (-in) \left(\frac{\partial f}{\partial x_\alpha} \right)_{kk} (P_\alpha^{n-1})_{kk} - i \left(\frac{\partial f}{\partial x_\alpha} \right)_{kk} (P_\alpha^n)_{kk}$$

$$= -i (n+1) \left(\frac{\partial f}{\partial x_\alpha} \right)_{kk} (P_\alpha^n)_{kk} \, , \tag{5A.13}$$

which is exactly the right-hand side of (5A.11). So we have proved that (5A.9) is true for any value of n. This proves the relations (5A.5) and (5A.4) as well.

Now put $f(r) = H_p$ in (5A.4). This gives us $D^{(0)}_{kk}$:

$$D^{(0)}_{kk} = -e \left[\rho_0, \sum_{\underline{q}} \frac{\rho_{\underline{q}} \cdot (\underline{r} - \underline{q})}{|\underline{r} - \underline{q}|^3} \right]_{kk} = -e \left[\nabla \sum_{\underline{q}} \frac{\rho_{\underline{q}} \cdot (\underline{r} - \underline{q})}{|\underline{r} - \underline{q}|^3} \right]_{kk} \cdot \left[\rho_0, \underline{r} \right]_{kk} \, . \tag{5A.14}$$

In Appendix 5B we show that

$$\left[-\nabla \sum_{\underline{q}} \frac{\rho_{\underline{q}} \cdot (\underline{r} - \underline{q})}{|\underline{r} - \underline{q}|^3} \right]_{kk} = \underline{E}_1 \, , \tag{5A.15}$$

where E_1 is the depolarization field for free electrons.

Therefore (5A.14) takes the form

$$D^{(0)}_{kk} = e\,\underset{\sim}{E}_1 \cdot [\rho_0, \underset{\sim}{r}]_{kk} = e\,E_{1\alpha}[\rho_0, x_\alpha]_{kk} = -ie\,E_{1\alpha}\left(\frac{\partial \rho_0}{\partial p_\alpha}\right)_{kk} . \tag{5A.16}$$

Using the previous notation

$$\left(\frac{\partial \rho_0}{\partial p_\alpha}\right)_{kk} = \frac{\partial \rho_k}{\partial k_\alpha} , \tag{5A.17}$$

[see equations (5.44) and (5.45)], (5A.16) becomes

$$D^{(0)}_{kk} = -ie\,E_{1\alpha}\frac{\partial \rho_k}{\partial k_\alpha} , \tag{5A.18}$$

which partly proves (5A.1). To prove it completely we must show that $D^{(0)}_{kk'}\,(k \neq k') = 0$:

$$D^{(0)}_{kk}\,(k \neq k') = -e\left[\rho_0, \sum \frac{\rho_{\underset{\sim}{q}} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3}\right]_{kk'} = 0 . \tag{5A.19}$$

To prove (5A.19) we expand the sum potential in a Maclaurin* series and use the induction method again :

$$f(\underset{\sim}{r}) = \sum_{\underset{\sim}{q}} \frac{\rho_{\underset{\sim}{q}} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3} = f(0) + x_\alpha f_{x_\alpha}(0) + \frac{x_\alpha x_\beta}{2!} f_{x_\alpha x_\beta}(0) + \cdots , \tag{5A.20}$$

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*Here one might ask whether the above potential is analytic at $\underset{\sim}{r} = \underset{\sim}{q}$. It can be shown, by considering $\rho_{\underset{\sim}{q}}$ as two point charges q and $-q$ with a distance d , that the potential at $\underset{\sim}{r} = \underset{\sim}{q}$ is analytic and takes the value of zero.

where

$$f_{x_\alpha} = \frac{\partial f}{\partial x_\alpha} \quad , \quad f_{x_\alpha x_\beta} = \frac{\partial^2 f}{\partial x_\alpha \partial x_\beta} \; , \quad \cdots \quad \text{etc.}$$

So for a general term (for example n^{th}) we must show that :

$$\left[\rho_0 , \, x_\alpha^n \right]_{kk'} \left(\underset{\sim}{k} \neq \underset{\sim}{k}' \right) = 0 \; . \tag{5A.21}$$

For $n=1$, the left-hand side of (5A.21) becomes

$$\underset{(\underset{\sim}{k} \neq \underset{\sim}{k}')}{\left[\rho_0 , \, x_\alpha \right]_{kk'}} = -\frac{1}{i} \underset{(\underset{\sim}{k} \neq \underset{\sim}{k}')}{\left(\frac{\partial \rho_0}{\partial p_\alpha} \right)_{kk'}} = -\frac{1}{i} K_0 \frac{\beta}{m} \left(p_\alpha \, e^{-\beta \frac{p_\alpha^2}{2m}} \right)_{kk'} \; , \tag{5A.22}$$

which is zero for $\underset{\sim}{k} \neq \underset{\sim}{k}'$. So for $n=1$ (5A.21) holds. Now assume that (5A.21) is true for any n and prove that it is also true for $(n+1)$, i.e:

$$\underset{(\underset{\sim}{k} \neq \underset{\sim}{k}')}{\left[\rho_0 , \, x_\alpha^{n+1} \right]_{kk'}} \stackrel{?}{=} 0 \; . \tag{5A.23}$$

The left-hand side of (5A.23) can be written as

$$\left[\rho_0 , \, x_\alpha^{n+1} \right]_{kk'} = \left(\rho_0 \, x_\alpha^{n+1} - x_\alpha^{n+1} \, \rho_0 \right)_{kk'}$$

$$\equiv \left(\rho_0 \, x_\alpha^n \, x_\alpha - x_\alpha^n \, \rho_0 \, x_\alpha + x_\alpha^n \, \rho_0 \, x_\alpha - x_\alpha^n \, x_\alpha \, \rho_0 \right)_{kk'}$$

$$= \left\{ \left[\rho_0 , \, x_\alpha^n \right] x_\alpha \right\}_{kk'} + \left\{ x_\alpha^n \left[\rho_0 , \, x_\alpha \right] \right\}_{kk'}$$

$$= \sum_{\underset{\sim}{k}''} \left\{ \left[\rho_0 , \, x_\alpha^n \right]_{kk''} \left(x_\alpha \right)_{k''k'} + \left(x_\alpha^n \right)_{kk''} \left[\rho_0 , \, x_\alpha \right]_{k''k'} \right\} . \tag{5A.24}$$

From (5A.21) and (5A.22) we know that $[\rho_0, X_\alpha^n]$ and $[\rho_0, X_\alpha]$ have only diagonal elements. Therefore (5A.24) becomes

$$[\rho_0, X_\alpha^{n+1}]_{\substack{kk' \\ (k\neq k')}} = [\rho_0, X_\alpha^n]_{kk} (X_\alpha)_{kk} + (X_\alpha^n)_{kk'} [\rho_0, X_\alpha]_{k'k'} \quad . \tag{5A.25}$$

In Appendix 5C we show that the off-diagonal elements of X_α are zero :

$$(X_\alpha)_{kk'} \ (\underset{\sim}{k} \neq \underset{\sim}{k}') = 0 \quad , \tag{5A.26}$$

which results in

$$(X_\alpha^n)_{kk'} \ (\underset{\sim}{k} \neq \underset{\sim}{k}) = 0 \quad . \tag{5A.27}$$

With (5A.26) and (5A.27), (5A.25) becomes

$$[\rho_0, X_\alpha^{n+1}]_{\substack{kk' \\ (\underset{\sim}{k}\neq\underset{\sim}{k}')}} = 0 \quad , \tag{5A.28}$$

which proves (5A.23). So we have proved that (5A.21) is true for any value of n . This proves the relation (5A.19) as well :

$$D^{(o)}_{kk'} \ (\underset{\sim}{k} \neq \underset{\sim}{k}') = -e \left[\rho_0 , \sum_{\underset{\sim}{g}} \frac{\underset{\sim}{\rho_g} \cdot (\underset{\sim}{r} - \underset{\sim}{g})}{|\underset{\sim}{r} - \underset{\sim}{g}|^3} \right]_{\substack{kk' \\ (\underset{\sim}{k}\neq\underset{\sim}{k}')}} = 0 \quad . \tag{5A.29}$$

Combining (5A.18) and (5A.29) we can write

$$D^{(o)}_{kk'} = -ie E_\alpha \frac{\partial \rho_k}{\partial k_\alpha} \delta_{kk'} \quad , \tag{5A.30}$$

which is exactly (5A.1).

To prove (5A.2) we follow the same method in the ℓ representation. As long as we carry out the calculation for the same band (we use

the diagonality of ρ_α , which holds for the same band, see Appendix 5C) we will have equations which are formally identical except that $\underset{\sim}{k}$ is replaced everywhere by ℓ . Since all the algebra is identical we only state the result:

$$D^{(o)}_{\ell\ell'} = -i e E_{1\alpha} \frac{\partial \rho_\ell}{\partial k_\alpha} , \qquad (5A.31)$$

where $\underset{\sim}{E}_1$ is the depolarization field defined for Bloch electrons.

Appendix 5B: Proof of the relation:

$$\left[\sum_{\underset{\sim}{q}} - \nabla_{\underset{\sim}{r}} \frac{\rho_{\underset{\sim}{q}} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3} \right]_{kk} = \underset{\sim}{E}_1 \quad . \tag{5B.1}$$

The microscopic field, $\underset{\sim}{E}_{mic}$, at the position $\underset{\sim}{r}$ is given by

$$\underset{\sim}{E}_{mic} = \underset{\sim}{E}_0 + \sum_{\underset{\sim}{q}} - \nabla_{\underset{\sim}{r}} \frac{\rho_{\underset{\sim}{q}} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3} \quad . \tag{5B.2}$$

The macroscopic field $\underset{\sim}{E}_{mac}$ is defined as the average of $E_{mic}(r)$ over the volume of the unit cell :

$$\underset{\sim}{E}_{mac} = \frac{1}{\Delta} \int_{\Delta} d^3 \underset{\sim}{r}\, \underset{\sim}{E}_{mic}(\underset{\sim}{r}) = \frac{1}{\Delta} \int_{\Delta} d^3 \underset{\sim}{r} \left[\underset{\sim}{E}_0 + \sum_{\underset{\sim}{q}} - \nabla \cdot \frac{\underset{\sim}{p}_{\underset{\sim}{q}} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3} \right] \tag{5B.3}$$

or

$$\begin{aligned} \underset{\sim}{E}_{mac} &= \underset{\sim}{E}_0 + \frac{1}{\Delta} \int_{\Delta} \sum_{\underset{\sim}{q}} - \nabla_{\underset{\sim}{r}} \frac{\underset{\sim}{p}_{\underset{\sim}{q}} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3} d^3 \underset{\sim}{r} \\ &= \underset{\sim}{E}_0 + \left\langle \underset{\sim}{E}_1(r) + \underset{\sim}{E}_2(r) + \underset{\sim}{E}_3(r) \right\rangle \quad . \end{aligned} \tag{5B.4}$$

Using the results of chapter I, namely $\left\langle \underset{\sim}{E}_1(r) \right\rangle = \underset{\sim}{E}_1$ and $\left\langle \underset{\sim}{E}_2(r) + \underset{\sim}{E}_3(r) \right\rangle = 0$, the expression (5B.4) becomes

$$\underset{\sim}{E}_1 = \frac{1}{\Delta} \int_{\Delta} \sum_{\underset{\sim}{q}} - \nabla_{\underset{\sim}{r}} \frac{\underset{\sim}{p}_{\underset{\sim}{q}} \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3} d^3 \underset{\sim}{r} \quad . \tag{5B.5}$$

Now consider the left-hand side of (5B.1):

$$\left[\sum_{\underset{\sim}{R}} -\nabla_r \frac{\underset{\sim}{R}\cdot(\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3}\right]_{kk} = \frac{1}{\Omega}\int e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}} \sum_{\underset{\sim}{R}} -\nabla_r \frac{\underset{\sim}{R}\cdot(\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3} e^{i\underset{\sim}{k}\cdot\underset{\sim}{r}} d^3r$$

$$= \frac{1}{\Omega}\int_{\Omega} \sum_{\underset{\sim}{R}} -\nabla_r \frac{\underset{\sim}{R}\cdot(\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3} dr = \frac{N}{N\Delta}\int_{\Delta} \sum_{\underset{\sim}{R}} -\nabla_r \frac{\underset{\sim}{R}\cdot(\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3} d^3r$$

$$= \frac{1}{\Delta}\int_{\Delta} \sum_{\underset{\sim}{R}} -\nabla_r \frac{\underset{\sim}{R}\cdot(\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3} d^3r \quad , \tag{5B.6}$$

which is the average value of the dipole field over the unit cell. Here we used the fact that the integrand is a periodic function.

Now comparing (5B.5) and (5B.6) we see that

$$\left[\sum_{\underset{\sim}{R}} -\nabla_r \frac{\underset{\sim}{R}\cdot(\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3}\right]_{kk} = \underset{\sim}{E}_1 \quad . \tag{5B.7}$$

Now consider the Bloch-wave case:

In this case the macroscopic quantity should be defined as the weighted average of the microscopic quantity over the unit cell :

$$\underset{\sim}{E}_{mac} = \frac{1}{\Delta}\int_{\Delta} d^3r\, |\phi_{nk}|^2 \underset{\sim}{E}_{mic}(r) = \frac{1}{\Delta}\int d^3r\, |U_{nk}|^2 \underset{\sim}{E}_{mic}(r) \quad . \tag{5B.8}$$

Substituting (5B.2) in (5B.8) we write

$$\underset{\sim}{E}_{mac} = \frac{1}{\Delta}\int d^3r\, |U_{nk}|^2 \left[\underset{\sim}{E}_0 + \sum_{\underset{\sim}{R}} -\nabla_r \frac{\underset{\sim}{R}\cdot(\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3}\right]$$

$$= \underset{\sim}{E}_0 \frac{1}{\Delta}\int_{\Delta} |U_{nk}|^2 d^3r + \frac{1}{\Delta}\int_{\Delta} d^3r\, |U_{nk}|^2 \sum_{\underset{\sim}{R}} -\nabla_r \frac{\underset{\sim}{R}\cdot(\underset{\sim}{r}-\underset{\sim}{R})}{|\underset{\sim}{r}-\underset{\sim}{R}|^3}$$

or

$$E_{mac} = E_0 + \frac{1}{\Delta}\int d^3r\, |U_{nk}|^2 \sum_{\underset{\sim}{g}} -\nabla_r \frac{f_g\cdot(r-g)}{|r-g|^3} \quad , \tag{5B.9}$$

where we have used that periodic parts of the Bloch wave functions are normalized in the unit cell. Now consider

$$\left[\sum_{\underset{\sim}{g}} -\nabla_r \frac{f_g\cdot(r-g)}{|r-g|^3}\right]_{ll'} = \frac{1}{\Omega}\int_{\Omega} e^{-ik\cdot r} U^*_{nk} \sum_{\underset{\sim}{g}} -\nabla_r \frac{f_g\cdot(r-g)}{|r-g|^3} e^{ik\cdot r} U_{nk}\, d^3r$$

$$= \frac{1}{\Omega}\int_{\Omega} |U_{nk}|^2 \sum_{\underset{\sim}{g}} -\nabla_r \frac{f_g\cdot(r-g)}{|r-g|^3}\, d^3r$$

$$= \frac{1}{\Delta}\int_{\Delta} |U_{nk}|^2 \sum_{\underset{\sim}{g}} -\nabla_r \frac{f_g\cdot(r-g)}{|r-g|^3}\, d^3r \quad ; \tag{5B.10}$$

here again we have used that the integrand is a periodic function.

Comparing (5B.9) and (5B.10) we see that

$$\left[\sum_{\underset{\sim}{g}} -\nabla_r \frac{f_g\cdot(r-g)}{|r-g|^3}\right] = E_1 \quad . \tag{5B.11}$$

Appendix 5C: The matrix elements of position and momentum operator.

a) plane wave representation:

$$\langle k | X_\alpha | k' \rangle = \frac{1}{\Omega} \int e^{-i k \cdot r} x_\alpha \, e^{i k' \cdot r} \, d^3 r \quad . \tag{5C.1}$$

It is known that, as a result of the uncertainty principle the matrix elements for $k = k'$ are not defined (infinite uncertainty!). However for $k \neq k'$ (5C.1) can be written as

$$\langle k | X_\alpha | k' \rangle = \frac{1}{\Omega} \int e^{-i k \cdot r} \frac{1}{i} \frac{\partial e^{i k' \cdot r}}{\partial k'_\alpha} d^3 r = \frac{1}{\Omega} \frac{\partial}{\partial k_\alpha} \int e^{i (k - k') \cdot r} \, d^3 r$$

$$= i \frac{\partial}{\partial k_\alpha} \delta_{kk'} \quad . \tag{5C.2}$$

Therefore the off-diagonal elements of X_α are zero :

$$(X_\alpha)_{kk'} \quad (k \neq k') = 0 \quad . \tag{5C.3}$$

Now consider the momentum operator :

$$\langle k | P_\alpha | k' \rangle = \frac{1}{\Omega} \int e^{-i k \cdot r} \frac{1}{i} \frac{\partial e^{i k' \cdot r}}{\partial x_\alpha} d^3 r$$

$$= k'_\alpha \frac{1}{\Omega} \int e^{i (k' - k) \cdot r} d^3 r = k_\alpha \delta_{kk'} \quad . \tag{5C.4}$$

Therefore P_α is a diagonal operator in plane wave representation.

From (5C.4) we can write

$$\left(P_\alpha^n \right)_{kk'} = \left(P_\alpha \right)^n_{kk'} \quad . \tag{5C.5}$$

b) Bloch-wave representation:

$$\langle n\underset{\sim}{k}|\, x_\alpha \,|n'\underset{\sim}{k}'\rangle = \frac{1}{\Omega}\int_\Omega e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, u^*_{nk}(\underset{\sim}{r})\, x_\alpha\, e^{i\underset{\sim}{k}'\cdot\underset{\sim}{r}}\, u_{n'k'}(\underset{\sim}{r})\, d^3r \qquad (5C.6)$$

Again for $n = n'$ and $k = k'$ the matrix elements of x_α do not exist. However for off-diagonal elements (5C.6) can be written as

$$\langle n\underset{\sim}{k}|\, x_\alpha \,|n'\underset{\sim}{k}'\rangle = \frac{1}{\Omega}\int_\Omega e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, u^*_{nk}(\underset{\sim}{r})\, \frac{1}{i}\frac{\partial e^{i\underset{\sim}{k}'\cdot\underset{\sim}{r}}}{\partial k'_\alpha}\, u_{n'k'}(\underset{\sim}{r})\, d^3r$$

$$= \frac{1}{\Omega}\int_\Omega e^{-i\underset{\sim}{k}\cdot\underset{\sim}{r}}\, u^*_{nk}(\underset{\sim}{r})\, \frac{1}{i}\left[\frac{\partial}{\partial k'_\alpha}\left(e^{i\underset{\sim}{k}'\cdot\underset{\sim}{r}}\, u_{n'k'}\right) - e^{i\underset{\sim}{k}'\cdot\underset{\sim}{r}}\frac{\partial u_{n'k'}}{\partial k'_\alpha}\right] d^3r$$

$$= \frac{1}{i}\frac{\partial}{\partial k'_\alpha}\,\frac{1}{\Omega}\int \phi^*_{nk}\,\phi_{n'k'}\, d^3r + \frac{i}{\Omega}\int_\Omega e^{i(\underset{\sim}{k}'-\underset{\sim}{k})\cdot\underset{\sim}{r}}\, u^*_{nk}\,\frac{\partial u_{n'k'}}{\partial k'_\alpha}\, d^3r$$

$$= -i\,\frac{\partial}{\partial k'_\alpha}\left(\delta_{nn'}\,\delta_{kk'}\right) + \frac{i}{\Omega}\int_\Omega e^{i(\underset{\sim}{k}'-\underset{\sim}{k})\cdot\underset{\sim}{r}}\, u^*_{nk}\,\frac{\partial u_{n'k'}}{\partial k'_\alpha}\, d^3r \,. \qquad (5C.7)$$

However, the fact that the $u_{nk}(\underset{\sim}{r})$ are periodic means that the exponential factor will cause the remaining integral to vanish unless $\underset{\sim}{k} = \underset{\sim}{k}'$. Thus

$$\langle n\underset{\sim}{k}|\, x_\alpha \,|n'\underset{\sim}{k}'\rangle = i\,\delta_{nn'}\frac{\partial}{\partial k_\alpha}\,\delta_{kk'} + i\, I^{nn'}_\alpha(\underset{\sim}{k})\,\delta_{kk'} \,, \qquad (5C.8)$$

where $I^{nn'}_n(\underset{\sim}{k})$ is defined by

$$I^{nn'}_\alpha(\underset{\sim}{k}) = \frac{1}{\Omega}\int u^*_{nk}\,\frac{\partial u_{n'k}}{\partial k_\alpha}\, d^3r \,. \qquad (5C.9)$$

In Appendix 5D we show that $I_\alpha^{nn'}(\underline{k})$ vanishes. Therefore the matrix elements of X_α in the same band (that is intraband matrix elements) are

$$\langle n\underline{k} | X_\alpha | n\underline{k}' \rangle = i \frac{\partial}{\partial k_\alpha} \delta_{kk'} \quad , \tag{5C.10}$$

which is zero for $\underline{k} \neq \underline{k}'$.

Next consider the momentum operator. The momentum operator can be written as

$$P_\alpha = m v_\alpha = mi \left[H_T, X_\alpha \right] = mi \left[H_0, X_\alpha \right] \quad , \tag{5C.11}$$

where v_α is the velocity operator. The diagonal elements of P_α are

$$(P_\alpha)_{\ell\ell} = mi \left[H_0, X_\alpha \right]_{\ell\ell} = m \left(\frac{\partial H_0}{\partial P_\alpha} \right)_{\ell\ell} = m \frac{\partial \varepsilon_\ell}{\partial k_\alpha} \quad . \tag{5C.12}$$

To calculate the off-diagonal elements we write (5C.11) as

$$P_\alpha = mi \left(H_0 X_\alpha - X_\alpha H_0 \right) \quad , \tag{5C.13}$$

which yields

$$\langle n\underline{k} | P_\alpha | n'\underline{k}' \rangle = mi \left(\varepsilon_\ell - \varepsilon_{\ell'} \right) \langle nk | x_\alpha | n'k' \rangle \quad . \tag{5C.14}$$

Substitution of (5C.8) into (5C.14) gives

$$\langle n\underline{k} | P_\alpha | n'\underline{k}' \rangle = -m \left(\varepsilon_{nk} - \varepsilon_{n'k} \right) \left[\delta_{nn'} \frac{\partial}{\partial k_\alpha} + I_\alpha^{nn'} \right] \delta_{kk'} \quad . \tag{5C.15}$$

We consider (5C.12) and (5C.15) to write down the intra-band matrix elements :

$$\langle n\underline{k}| p_\alpha | n\underline{k}' \rangle = m \frac{\partial \varepsilon_e}{\partial k_\alpha} \delta_{kk'} , \qquad (5C.16)$$

which is zero for $\underline{k} \neq \underline{k}'$.

Appendix 5D: Symmetry properties:

We consider here the symmetry properties of the various matrix elements with respect to the eigenfunctions ϕ_{nk} of H_o.

Consider the Schrödinger equation

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\underline{r})\right]\phi_{nk}(\underline{r}) = E_{nk}\,\phi_{nk} \,. \tag{5D.1}$$

With substitution of $\phi_{nk}(\underline{r}) = \frac{1}{\Omega^{1/2}} e^{i\underline{k}\cdot\underline{r}}\, U_{nk}(\underline{r})$ we obtain

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\underline{r})\right] e^{i\underline{k}\cdot\underline{r}}\, U_{nk}(\underline{r}) = E_{nk}\, e^{i\underline{k}\cdot\underline{r}}\, U_{nk}(\underline{r}) \,. \tag{5D.2}$$

By writing $\nabla^2 = div\,(grad_r)$, (5D.2) reduces to

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + \frac{\hbar^2\underline{k}}{im}\cdot grad_r + \frac{\hbar^2k^2}{2m} + V(\underline{r})\right] U_{nk}(\underline{r}) = E_{nk}\, U_{nk}(\underline{r}) \,. \tag{5D.3}$$

From (5D.3) it is seen that

$$U^{*}_{n,-k} = U_{n,k} \tag{5D.4}$$

and

$$U_{n,-k}(-r) = U_{n,k}(r) \,. \tag{5D.5}$$

Consider $I_\alpha^{nn'}(k)$. By using (5D.4) and (5D.5), we can write

$$I_\alpha^{nn'}(k) = \int U^{*}_{nk}(\underline{r})\,\frac{\partial U_{n'k}(\underline{r})}{\partial k_\alpha}\,d^3r = \int U^{*}_{nk}(-\underline{r})\,\frac{\partial U_{n'k}(-\underline{r})}{\partial k_\alpha}\,d^3r$$

$$= \int u^{*}_{n,-k}(r)\, \frac{\partial u_{n'-k}(r)}{\partial k_\alpha}\, d^3r = \int u_{nk}(r)\, \frac{\partial u^{*}_{n'k}(r)}{\partial k_\alpha}\, d^3r$$

$$= -\int \frac{\partial u_{nk}}{\partial k_\alpha}\, u^{*}_{n'k}\, d^3r = -I^{n'n}(k) \,.$$

(5D.6)

Here we have used the identity

$$\int \frac{\partial u_{nk}}{\partial k_\alpha}\, u^{*}_{n'k}\, d^3r = -\int u_{nk}\, \frac{\partial u^{*}_{n'k}}{\partial k_\alpha}\, d^3r \,,$$

(5D.7)

which results from the following relation :

$$\frac{\partial}{\partial k_\alpha}\left[\int u_{nk}\, u^{*}_{n'k}\, d^3r\right] = 0 \,,$$

(5D.8)

since the u_{nk} are orthonormal.

From (5D.6) we deduce that the diagonal elements, $I^{nn}_{\alpha}(k)$, vanish identically:

$$I^{nn}_{\alpha}(k) = 0 \,.$$

(5D.9)

APPENDIX 5E

HIGHER APPROXIMATION TO THE DENSITY MATRIX

The problem of finding the higher order corrections to the density matrix will now be considered. To obtain these, one need only continue the iterative process begun in section (5.3). It was found that to the first order in E_α the equation obeyed by the diagonal elements of the density matrix is

$$0 = e\, E_{mac\alpha} \frac{\partial f_k}{\partial k_\alpha} + \sum_{k'(\neq k)} \left(W^{(0)}_{k'k} f_k - W^{(0)}_{kk'} f_{k'} \right) . \tag{5E.1}$$

Before going into the details of this appendix we note that the higher order corrections will be irrelevant to the present scattering mechanism since it employs only elastic collisions[44]. An exact method should include inelastic collisions as well. To do so, following Argyres[45], we write the collision term of (5E.1) with the exclusion factors, i.e.,

$$0 = e\, E_{mac\alpha} \frac{\partial f_k}{\partial k_\alpha} + \sum_{k'(\neq k)} \left[W_{k'k} f_k (1-f_{k'}) - W_{kk'} f_{k'} (1-f_k) \right] \tag{5E.2}$$

Once the scattering mechanism is known, f_k can be solved from (5E.2). Let us denote the solution of (5.5-2) by $f(k, E_{mac})$:

$$f_k = f(k, E_{mac}) . \tag{5E.3}$$

To proceed further we consider the equation to the second order in E_α obeyed by the density matrix:

$$i \frac{\partial \rho_2}{\partial t} = [H_1, \rho_2] + [H_F + H_D, \rho_F] , \tag{5E.4}$$

ρ_F satisfying (5.25). Using (5.27), (5.28) and (5.29), (5E.4) becomes.

$$i\frac{\partial \rho_2}{\partial t} = [H, \rho_2] + [H_B + H_\rho, f]\, e^{2st} . \tag{5E.5}$$

(5E.5) has the solution

$$\rho_2 = g\, e^{2st} , \tag{5E.6}$$

yielding

$$2is\, g = [H, g] + [H_B + H_\rho, f] . \tag{5E.7}$$

In the plane wave representation (5E.7) becomes

$$(\omega_{kk'} - 2is)\, g_{kk'} = C_{2kk'} + D_{2kk'} + \sum_{k''} \left(g_{kk''} H'_{k''k'} - H'_{kk''} g_{k''k'} \right) \tag{5E.8}$$

where $C_2 = [f, H_B]$ and $D_2 = [f, H_\rho]$.

The method of solution of (5E.8) is the same as before, namely involving a split into diagonal and off-diagonal terms in k . We may then write

$$-2is\, g_k = C_{2k} + D_{2k} + \sum_{k' (\neq k)} \left(g_{kk'} H'_{k'k} - H'_{kk'} g_{k'k} \right) \tag{5E.9}$$

for $k = k'$, and

$$(\omega_{kk'} - 2is)\, g_{kk'} = C_{2kk'} + D_{2kk'} + (g_k - g_{k'}) H'_{kk'} + \sum_{k'' (\neq k, k')} \left(g_{kk''} H'_{k''k'} - H'_{kk''} g_{k''k'} \right) \tag{5E.10}$$

for $k \neq k'$. Here $g_k = g_{kk}$, $C_{2k} = C_{2kk}$ and $D_{2k} = D_{2kk}$. Again we solve these equations to the lowest

order in λ . To do so we investigate the λ dependence of the different terms for small λ . First we begin with the commutators C_2 and D_2 . In the lowest order we can write

$$C_2^{(0)} = \left[f^{(0)}, H_E \right] \propto \left[\rho_0 X_\alpha , X_\alpha \right] = \left[\rho_0 , X_\alpha \right] X_\alpha \qquad (5E.11)$$

and

$$D_2^{(0)} = \left[f^{(0)}, H_P \right] \propto \left[\rho_0 X_\alpha , H_P \right] = \left[\rho_0 , H_P \right] X_\alpha \ . \qquad (5E.12)$$

It is noted that the commutators on the right-hand sides of (5E.11) and (5E.12) are $C^{(0)}$ and $D^{(0)}$ respectively. Then the matrix elements of C_2 and D_2 become

$$C^{(0)}_{2kk'} \propto \sum_{\underset{\sim}{k''}} C^{(0)}_{kk''} (X_\alpha)_{k''k'} \propto C^{(0)}_{kk'} \qquad (5E.13)$$

and

$$D^{(0)}_{2kk'} \propto \sum_{\underset{\sim}{k''}} D^{(0)}_{kk''} (X_\alpha)_{k''k'} \propto D^{(0)}_{kk'} \ ; \qquad (5E.14)$$

here we have used the diagonality of X_α (see Appendix 5C). It was seen in section (5.3) that $C^{(0)}_{kk'}$ and $D^{(0)}_{kk'}$ are zero for $\underset{\sim}{k} \neq \underset{\sim}{k'}$. Thus $C^{(0)}_{2kk'}$ and $D^{(0)}_{2kk'}$ will be zero for $\underset{\sim}{k} \neq \underset{\sim}{k'}$. Hence the diagonal terms of C_2 and D_2 begin with zero'th order in λ while the off-diagonal ones are of the first order in λ . From the results of usual transport theory, again, we can say that g_k is of order of λ^{-2} . Hence from (5E.10), (5E.13) and (5E.14) $g_{kk'}$ is of order of λ^{-1} . Thus (5E.10) can be solved by an iterative procedure. From the orders in λ discussed above, we see that, on the right-hand side of (5E.10) the third term dominates and we obtain

$$g_{kk'} = \frac{(g_k - g_{k'})\, H'_{kk'}}{(\omega_{kk'} - 2is)} \tag{5E.15}$$

in lowest order. If we insert this in (5E.9) and retain only the lowest order, we obtain

$$-2is\, g_k = C_{2k} + D_{2k} + \sum_{k'(\neq k)} |H'_{kk'}|^2 \left[(g_k - g_{k'}) \left(\frac{1}{\omega_{kk'} - 2is} - \frac{1}{\omega_{kk'} + 2is} \right) \right] . \tag{5E.16}$$

To proceed further we try to find the matrix elements C_{2k} and D_{2k}. We may write

$$C_{2k} = [f, H_E]_{kk} = eE_{0\alpha} [f, X_\alpha]_{kk} = -eE_{0\alpha} i \left(\frac{\partial f}{\partial p_\alpha} \right)_{kk}$$

$$= -ieE_{0\alpha} \frac{\partial f_k}{\partial k_\alpha} \tag{5E.17}$$

and

$$D_{2k} = [f, H_P]_{kk} = -e \left[f, \sum_{\underset{\sim}{q}} \frac{P_q \cdot (\underset{\sim}{r} - \underset{\sim}{q})}{|\underset{\sim}{r} - \underset{\sim}{q}|^3} \right]_{kk}$$

$$= eE_{1\alpha} [f, X_\alpha]_{kk} = -ieE_{1\alpha} \left(\frac{\partial f}{\partial p_\alpha} \right)_{kk} = -ieE_{1\alpha} \frac{\partial f_k}{\partial k_\alpha} , \tag{5E.18}$$

here we have used the relations (5A.4) and (5A.15). Then substituting (5E.3) into $(C_{2k} + D_{2k})$ we get

$$C_{2k} + D_{2k} = -ie (E_{0\alpha} + E_{1\alpha}) \frac{\partial f(\underset{\sim}{k}, E_{max})}{\partial k_\alpha} . \tag{5E.19}$$

With (5E.19), equation (5E.16) becomes

$$-2is\, g_k = -ie\, E_{max\alpha} \frac{\partial f(\underset{\sim}{k}, E_{max})}{\partial k_\alpha}$$

$$+ \sum_{k'(\neq k)} |H'_{kk'}|^2 \left[(g_k - g_{k'}) \left(\frac{1}{\omega_{kk'} - 2is} - \frac{1}{\omega_{kk'} + 2is} \right) \right] . \tag{5E.20}$$

The second term on the right-hand side of (5E.20) has exactly the same form as the second term of the right-hand side of (5.52). Therefore carrying out the similar arguments* of section (5.3), (5E.20) can be written in the limit as $s \to 0$, as

$$0 = e^2 E_{mac\alpha} \frac{\partial f(k, E_{mac})}{\partial k_\alpha} + \left(\frac{\partial g_k}{\partial t}\right)_{coll} . \qquad (5E.21)$$

Equation (5E.21) corresponds to the transport equation second order in E_α . The first term is the acceleration term due to external field and the field of induced dipoles. The second term is just the rate of change of g_k due to collisions with randomly distributed impurities. From (5E.21) we again conclude that the net electric field appearing in the transport equation of second order in E_α (where the non-ohmic behaviour starts) is just the macroscopic electric field, E_{mac} .

One can continue the iterative procedure to solve the equation nth order in E_α :

$$i \frac{\partial \rho_n}{\partial t} = [H, \rho_n] + [H_F + H_0, \rho_{n-1}] , \qquad (5E.22)$$

the solution of which will have the form

$$\rho_n = g_n e^{nst}$$

where g_n , in general, is written as

$$g_n = g(\ell, E_{mac}^n) . \qquad (5E.23)$$

*In this case the assumption $s^{-1} \ll t_r$ is replaced with $(2s)^{-1} \ll t_r$ which shrinks the range of s .

From (5E.23) we conclude that, even in the non-ohmic region, in the presence of induced dipoles the net electric field appearing in the density matrix is just the macroscopic electric field. Hence the electric field appearing in all transport coefficients including the electric conductivity will be just the macroscopic field.

Conclusions and Suggestions for future studies:

We have investigated the effect of local field corrections on transport properties of solids. In the hopping limit the problem reduces to an evaluation of the dipolar energy difference at two sites $\underset{\sim}{q}$ and $\underset{\sim}{q}''$ involved in the site jump: The dipolar energy difference ($W_{\underset{\sim}{q}}^{\rho} - W_{\underset{\sim}{q}''}^{\rho}$) has been calculated for induced electronic polarization of an isotropic medium. Namely, the induced dipoles are assumed to be parallel and proportional to the applied field. For the crystalline case, when hopping takes place on the same sublattice, as a result of detailed cancellation of short-range and Lorentz contributions, the effect of ($W_{\underset{\sim}{q}}^{\rho} - W_{\underset{\sim}{q}''}^{\rho}$) vanishes. However, for hopping between different sublattices, it has been shown that local field corrections can exist. While negligible at low fields ($e\underset{\sim}{E}_0 \cdot (\underset{\sim}{q} - \underset{\sim}{q}'') < kT$), these can be considerable for high fields.

For glasses, as a result of short-range order, similar results have been obtained. Namely, no local field corrections for hopping between identical sites, but possible corrections for hopping between non-identical sites especially at high fields.

In the band limit when intra-band motion is considered, it turns out that [see equations (5.62) and (5.88)] in the presence of induced electronic dipoles, the net electric field appearing in the customary transport equation is just the macroscopic electric field unmodified by the local field corrections.

In the hopping limit, we have not considered the effect of random distributions of the dipoles in the crystalline or glass lattice. Neither have we considered the effect of the randomly oriented dipoles in the system. These will affect the present calculations, but should hopefully produce no qualitative changes as a result of ensemble and thermal averages. These cases will be considered at some future time.

In the band limit, the effect of inter-band transitions still remains to be examined. In this case we expect to have local field effects in line with the result for hopping between different sub-lattices and those of Wiser[6] for the atomic part of the dielectric constant.

REFERENCES

(1) Austin, J.G., and Sayer, M., J. Phys. C: Solid St. Phys. 7, 905 (1974).

(2) Schmid, A.P., J. App. Phys. 39, 3140 (1968).

(3) Greaves, G.N., J. Non-Cryst. Solids 11, 427 (1973).

(4) Tessman, J.R., Kohn, A.H., and Shockley, W., Phys. Rev. 92, 890 (1953).

(5) Adler, S.L., Phys. Rev. 126, 413 (1962).

(6) Wiser, N., Phys. Rev. 129, 62 (1963).

(7) Lidiard, A.B., Handbuch der Physik, 20, 246 (1957).

(8) Hoodless, I.M., Strange, J.H., and Wylde, L.E., J. Phys. C: Solid St. 4, 2742 (1971).

(9) Munn, R.W., Chem. Phys. Lett. 16, 429 (1972).

(10) Munn, R.W., and William, D.F., J. Chem. Phys. 59, 1742 (1973).

(11) Munn, R.W., J. Phys. C: Solid St. 8, 2721 (1975).

(12) Kohn, W., and Luttinger, J.M., Phys. Rev. 108, 590 (1957).

(13) Efros, A.F., Soviet Phys. Solid St. 9, 901 (1967).

(14) Klinger, H.I., J. Non-Cryst. Solids 4, 463 (1970).

(15) Bryxin, V.V., and Firsov, Yu.S., Proc. Tenth Int. Conf. on the Physics of Semiconductors, 767 (1970).

(16) Holstein, T., Ann. Phys. (N.Y.) 8, 325 (1959).

(17) Holstein, T., Ann. Phys. (N.Y.) 8, 343 (1959).

(18) Austin, I.G., and Mott, N.F., Advances in Physics, 18, 41 (1969).

(19) Friedman, L.R., and Holstein, T., Ann. Phys. 21, 494 (1963).

(20) Austin, I.G., J. Phys. C: Solid St. Phys. 5, 1687 (1972).

(21) Morse, P.M., and Feshbach, H., Methods of Theoretical Physics: International series in Pure and Applied Physics, New York (1953).

(22) Sağlam, M., and Friedman, L., J. Phys. C: Solid St. Phys. 8, L245 (1975).

(23) Mott, N.F., and Jones, H., The theory of the properties of metals and alloys. The international series of Monographs on Physics, Oxford, 1936.

(24) Becker, R., Electromagnetic Fields and Interactions, Blackie p.102 (1964).

(25) Slater, J.C., Phys. Rev. 78, 748 (1950).

(26) Miller, A., and Abrahams, E., Phys. Rev. 120, 745 (1960).

(27) Madelung, E., Die Math. Hifsmittel des Physikers, Dover publications, New York (1943).

(28) Luttinger, J.M., and Tisza, L., Phys. Rev. 70, 954 (1946); 72, 257 (1947).

(29) Sommerfeld, A., and Bethe, H., Handbuch der Physik (Edwards Brothers, Ann Arbor, 1943) Vol. 24, Part 2, pp. 499-554.

(30) Jones, H., and Zener, C., Proc. Roy. Soc. A 144, 101 (1934).

(31) Tolman, R.C., Principles of Statistical Mechanics (Oxford 1930) p.327.

(32) Thomas, R.B., Ph.D. thesis, Technical Information Series, R6 35059, (1963).

(33) Pollak, M., and Geballe, T.H., Phys. Rev. 122, 1742 (1961).

(34) Keller, F.J., and Murray, R.B., Phys. Rev. 150, 670 (1966).

(35) Gibbons, D.J., and Spear, W.E., J. Phys. Chem. Solids, 27, 1917 (1966).

(36) Anderson, P.W., Phys. Rev. 109, 1492 (1958).

(37) Ziman, J.M., Principles of the Theory of Solids, second edition, (Cambridge) pp. 271 (1972).

(38) Schiff, L.J., Quantum Mechanics (McGraw-Hill 1955).

(39) Pollak, M., Phys. Rev. 133 A 564 (1964).

(40) Pollak, M., Phys. Rev. 138 A 1822 (1965).

(41) Mott, N.F., Can. J. Phys. 34, 1356 (1956).

(42) Conwell, E.M., Phys. Rev. 103, 51 (1956).

(43) Sewell, G.L., Phys. Rev. 129, 597 (1963).

(44) Conwell, E.M. High Field Transport in Semiconductors, Academic Press, New York/London (1967).

(45) Argyres, P.N. J. Phys. Chem. Solids, 19, 66 (1961).